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PHYSICAL REVIEW

X-RAY DIFFRACTION IN LIQUIDS: A COMPARISON OF ISOMERS OF NORMAL HEPTANE AND OF CERTAIN CARBON CHAINS

By G. W. Stewart

Abstract

With the $K\alpha$ doublet of molybdenum, diffraction ionization curves are reported on synthetic decane, 2–2–4 trimethyl pentane, 2 methyl hexylene 2 and the following eight isomers of normal heptane obtained from the Ethyl Gasoline Corporation: 2–2–3 trimethyl butane, 3–3, 2–3, 2–2 and 2–4 dimethyl pentane, 3 ethyl pentane, 3 methyl hexane, and 2 methyl hexane. The experiments are a continuation of those of Stewart and Morrow, Stewart, and Stewart and Skinner. The diffraction peak of synthetic decane occurs at precisely the same angle as of eight of the other normal paraffins containing from five to fifteen carbon atoms so that the diameter of the normal paraffin chain throughout this range, as computed by Bragg's diffraction law, is 4.64A. The experience with normal decane was a repetition of that with normal pentane previously reported by the author. The length of the chain is in agreement with the formula, $L=(1.24n+2.70)\times 10^{-8}$cm if n is the number of carbon atoms, and if the molecules may be regarded as longitudinally parallel and in square array in the plane normal to their lengths. The agreement is within less than one percent. With the exception of 2 methyl hexane wherein two diameters are found, and of 3 ethyl pentane which is a symmetrically branched structure, all the other heptane isomers, six in number, have diameters that are 1.04A larger than the normal paraffins. A consideration of this fact and of the alterations in density not in agreement with the formula just cited reach the conclusion that the molecular chains of the isomers are distorted either by bending or by another type of atom separation. A tentative conclusion is that the attachment of two CH_3 groups to the same atom may or may not increase the diameter by the same amount, this depending upon whether a third CH_3 branch is attached to an adjacent atom or to the next but one. The attachment of a CH_3 group on the next to end carbon atom seems, in the cases of 2 methyl hexane and 2 methyl hexylene 2, to produce two symmetrical branches of one CH_3 group each. Both this and the preceding conclusion are highly tentative but suggest the possibility of learning more of the nature of the chain by more extended experiments on isomers of normal paraffins. The foregoing experiments contribute not only to our knowledge of molecular structure but also to the evidence for the cybotactic state as one of importance in fundamental phenomena in liquids.

Introduction

IN a series of articles by Stewart and Morrow[1], Stewart and Skinner[2], Morrow[3] and Stewart,[4] evidence has been brought forward to indicate

[1] Stewart and Morrow, Phys. Rev. **30,** 232 (1927), and Proc. Nat. Acad. **13,** 222 (1927).
[2] Stewart and Skinner, Phys. Rev. **31,** 1 (1928).
[3] Morrow, Phys. Rev. **31,** 10 (1928).
[4] Stewart, Phys. Rev. **31,** 174 (1928), and Proc. Nat. Acad. **13,** p. 787 (1927).

that there is a molecular space arrangement in liquids, that this condition is important and in need of emphasis in the study of all fundamental liquid phenomena and that x-ray diffraction measurements in liquids are of value in the study of molecular structure. Incidentally such measurements have proved of distinct value in distinguishing between isomers of chain compounds. The reader is reminded of the view point of these contributions. The suggestion of a molecular space array in liquids is not new and is doubtless as old as crystalline theory itself. But the results of the experiments of this laboratory combined with general views concerning molecular forces, have brought the authors to the view that the ordered grouping of molecules is not crystalline, is unique in character and is worthy of a special name, "cybotaxis." The studies have not progressed to the point where the details of this cybotactic state may be stated. It is fairly evident, however, that the "straight" carbon chains with a carbon content of from one to fifteen atoms are arranged longitudinally parallel and with sufficient uniformity to give the effect of the existence at any instant of a large number of minute groups each of which is fairly regular. The orientation differs from point to point.[5] Indeed, the liquid state is a modified and exaggerated example of an "irregular crystal." Yet these somewhat regular minute groups, arranged irregularly among themselves, are not crystalline and differ fundamentally in that they are not in stable configuration. The view to be emphasized is that one should extrapolate, as it were, the conception of the arrangement of long molecules to short molecules. The cybotactic state continues to remain of importance with decreasing lengths of molecules even though the x-ray method of measurement becomes less effective. One should approach the liquid state from the conditions obtaining with long molecules in a liquid, and not from spherical molecules in the gaseous state. In the former case Bragg's diffraction law, $\lambda = 2d \sin(\theta/2)$ is used. In the latter the formula chosen is that originally derived by Ehrenfest[6] and by Debeye and Scherrer[7] and used by Keesom and Smedt,[8] Katz[9] and others,

[5] Sogani has independently adopted this view, as is shown in a paper, Indian Journal of Physics, Vol. II. p. 97, (1927). Katz, Zeits. f. Physik **46,** p. 392 (1928), also mentions this with distinctness.

[6] Ehrenfest, Proc. Amsterdam **17,** 1184 (1915).

[7] Debeye and Scherrer, Nachricthen Göttingen (1916). (See also P. Debeye Ann. d. Physik (4) **46,** p. 809 (1915).

[8] Keesom and Smedt, Proc. Amsterdam **25,** p. 118 (1922).

[9] Katz, Zeits. f. Physik **45,** 97 (1927).

[8] Stewart, Phys. Rev. **31,** 174 (1928).

[9] Dr. Calingaert describes the determination of the best values of densities as follows: In order to obtain the best values for d_4^{20} for the normal paraffin hydrocarbons from C^5 to C^{15}, the following method was used: the values given in International Critical Tables, and by R. E. Wilson and W. H. Bahlke in Industrial and Engineering Chemistry **16,** 115 (1924) were plotted on a scale of d_4^{20} versus "C", the number of carbon atoms in the molecule, reasonable correction being made where the values were not given at 20°. To these were added the value for n-butane given by L. I. Dana, Refrig. Eng. **12,** 387 (1926) and for n-pentane given by S. Young, and reported in Beilstein. A smooth curve was drawn through the points and the slope of that curve was also plotted against C. After smoothing out the slope curve, the corrections were reported to the density curve and the value read off the corrected curve. (The

wherein $\lambda = 2d \sin(\theta/2) \times 0.814$. This was originally derived for diatomic gas molecules, but gives consistent molecular volumes for short molecules if the assumption of closely packed spheres is made.

It is not the function of the current paper to give a resumé of the important work now being done in x-ray diffraction in liquids, but to continue the reports of the experimental results of this laboratory with the conclusions therefrom.

Normal Paraffins

In our earlier work[8] on normal paraffins, it was found that seven out of the nine normal paraffins had a diffraction peak at the same angle, namely 8.8°. The two expections were pentane and decane. When going to press, a sample of synthetic pentane, kindly prepared by the Eastman Kodak Company, was tested and found to have its diffraction peak at 8.8°. This new fact was added in a footnote. Since that time, through the courtesy of Dr. George Calingaert of the Ethyl Gasoline Corporation, a sample of synthetic decane was tested and found to have its diffraction peak at 8.8°. These alterations, shown in Fig. 1, are interesting for two reasons. They show the possibility of the x-ray diffraction as a method of distinguishing isomers from the normal paraffins and they prove that the normal paraffin chain has precisely the same "diameter" from pentane to pentadecane. This diameter is 4.64A if the diffraction peak is interpreted by Bragg's Law.

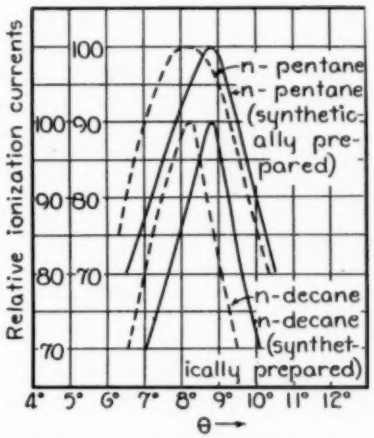


Fig. 1. Variation of diffraction-ionization curve with content of isomers.

Through the kindness of Dr. George Calingaert,[9] it is now possible to apply the best density values in computing the space occupied by the carbon atom in the chain. The density values for pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pentadecane are 0.627, 0.660, 0.684, 0.702, 0.718, 0.731, 0.751, 0.766, 0.772. Since the paraffin chain is symmetrical, it is reasonable to assume that the molecules are arranged with lengths parallel and in a square array in a plane perpendicular thereto. The length of the chain can then be expressed by the formula,

$$L = \frac{(\text{Molecular weight}) \times (\text{Mass of } H \text{ atom})}{(4.64 \times 10^{-8})^2 \times \text{density}} \qquad (1)$$

When these values are plotted, it is found that, with a variation of less than

large discrepancies with some values given in I.C.T. are probably due to the fact that these values are not d_4^{20} as reported, but more likely d^{15} for pentane, and d° for decane and dodecane.)

1 percent, these lengths correspond to the following formula, expressed in Ångstroms or 10^{-8} cm,

$$L=1.24n+2.70 \qquad (2)$$

wherein n is the number of carbons in the chain and 2.70×10^{-8} is the length occupied by the two H atoms at the terminals of the chain. As stated in the earlier article,[8] Müller and Saville[10] found a length of 1.3A* for each additional CH_2 in solid hydrocarbons and Piper, Brown and Dyment[11] found a

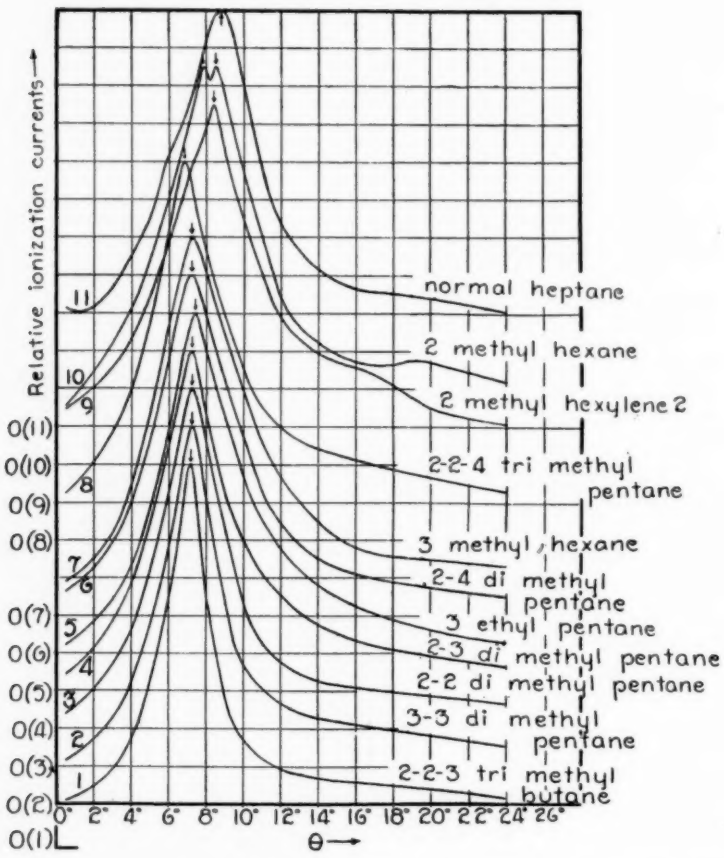


Fig. 2. Ionization-diffraction curves for n-heptane, eight isomers, an octane and 2 methyl hexylene 2.

length of 1.22A. If instead of a square array the densest packing were assumed, the volume occupied would be $L'\times4.63\times4.63 \sin 60°\times10^{-16}$ and L' would be 15 percent greater than L. But in view of the measurements on solid hydrocarbons the assumption of a square array seems justified.

[10] Müller and Saville, Jl. Chem. Soc. **27**, 509 (1925).

* A is used for Ångstroms or 10^{-8} cm.

[11] Piper, Brown and Dyment, Chem. Soc. Jl. **127**, 2194 (1925).

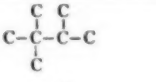
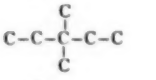
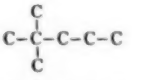
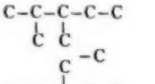
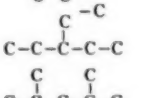
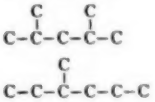
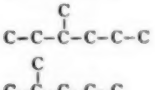
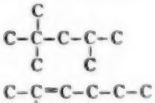
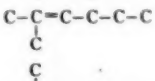
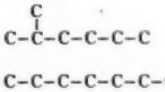
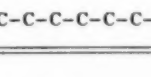
Method and Experimental Results

There has been no material alteration of the method or equipment as described in the previous papers from this laboratory to which reference has been made. In Fig. 2 are shown the ionization diffraction angle curves for the following: 2-2-3 trimethyl butane, 3-3 dimethyl pentane, 2-2 dimethyl pentane, 2-3 dimethyl pentane, 3 ethyl pentane, 2-4 dimethyl pentane, 3 methyl hexane, 2-2-4 trimethyl pentane, 2 methyl hexylene 2, 2 methyl hexane, and normal heptane. Nine of these are heptanes and one an octane, and the 2 methyl hexylene 2 is added for the purpose of a desired comparison.

Discussion of Derived Results

In Table I are given the results obtained from the curves in Fig. 2, using Bragg's Law $\lambda = 2d \sin(\theta/2)$ and the wave-length of the approximately monochromatic beam 0.712A.

Table I. *Structure and diameters of molecules.*

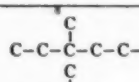
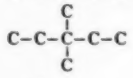
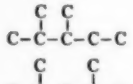
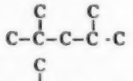
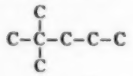
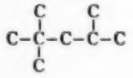
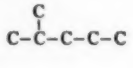
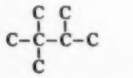
Name	Structure	Diameter in 10^{-8} cm	Increase in diam. in 10^{-8} cm	Width of Peak
(1) 2–2–3 Trimethyl butane		5.69	$1.05 \pm .05$	1.7°
(2) 3–3 Dimethyl pentane		5.68	$1.04 \pm .05$	2.4°
(3) 2–2 Dimethyl pentane		5.68	$1.04 \pm .05$	2.8°
(4) 2–3 Dimethyl pentane		5.68	$1.04 \pm .05$	2.8°
(5) 3 Ethyl pentane		5.51	$0.87 \pm .05$	3.2°
(6) 2–4 Dimethyl pentane		5.68	$1.04 \pm .05$	3.6°
(7) 3 Methyl Hexane		5.68	$1.04 \pm .05$	3.5°
(8) 2–2–4 Trimethyl pentane		6.00	$1.37 \pm .05$	2.8°
(9) 2 Methyl Hexylene 2		4.85	$0.21 \pm .05$	3.6°
(10) 2 Methyl hexane		5.25 4.84	$0.61 \pm .05$ 0.20	4.3°
(11) Normal heptane		4.64	$0.00 \pm .05$	3.6°

(1) *General remarks.* Of the heptanes, there is one unusual case, 2 methyl hexane, wherein two diameters are found. With this exception, there are only two alterations in diameter for seven isomers. Six of them have an increase in diameter of 1.04A and one of 0.87A. A comparison of the struc-

tural differences in the molecules can hardly be said to account for this similarity. For example, one CH_3 and two CH_3 branches attached to the same atom or to different atoms seem to have the same effect upon the diameter. If a comparison is made with the alcohol isomers, it is found that 1.04A is roughly twice the increase in diameter of an alcohol chain when CH_3 or OH is attached as a branch. Also, the consistency in the results of the alcohol isomers seems to be not so much in existence here. The difference in the results for the paraffin and alcohol isomers is probably caused by a difference in the distortion of the two chains. The case of 2 methyl hexane will be discussed at a later point.

(2) *Distortion of chains.* As noted in a previous paragraph, the assumption of a square array of the normal paraffin molecules gives entirely consistent values for the length in the chain of the carbon atoms and of the terminal hydrogen atoms. Much confidence can be placed in these values because they agree for the nine normal paraffins to within a variation of less than 1 percent. The "straight" portion of the chains with the isomers should have the same values for the carbon and hydrogen atom lengths or the chain may be said to be distorted. If the square array is now assumed, it is possible to compare the lengths of the isomer chains, obtained by the measurements of diameters and the use of an equation of the form of (1), with the lengths computed by Eq. (2). They will be denoted by L_1 and L_2 respectively. The results are given in Table II. There is also included an octane, 2-2-4 trimethyl pentane.

TABLE II. *Variation of L from computed value.*

Name	Structure	L_2	L_1	L_2-L_1	$(L_2-L_1)/L_2$
3 Methyl hexane		10.14	7.46	2.68	25.4
3-3 Dimethyl pentane		8.90	7.38	1.52	17.1
2-3 Dimethyl pentane		8.90	7.38	1.52	17.1
2-4 Dimethyl pentane		8.90	7.61	1.29	14.5
2-2 Dimethyl pentane		8.90	7.61	1.29	14.5
2-2-4 Trimethyl pentane		8.90	7.54	1.36	15.3
2 Methyl hexane		10.14 10.14 9.61	10.47 8.87 9.63	+.33 1.27 0.00	−3.1 12.5 0.0
2-2-3 Trimethyl butane		7.66	7.45	.21	2.7

The last column shows that the lengths are from 25 to 2.7 percent (2 methyl hexane excepted) less than they should be if undistorted. Hence the conclusion favors definite distortion. But a further examination shows that there are two corroborating points. First, the greatest distortion is that of 3 methyl hexane, and the structure of the molecule, with a CH_3 branch on one side and near the center, is favorable to distortion. Second, the one having the least distortion, 2-2-3 trimethyl butane, is the shortest molecule of the group, is one of the best balanced against distortion, and Fig. 2 shows that it gives distinctly the sharpest peak of any of the compounds there shown. In fact, it has one of the sharpest liquid peaks yet found in this laboratory. That it may be well balanced against distortion is recognized if one makes the reasonable assumption that the carbon atoms are not in a straight chain and the three branches are not in the same plane.

Table II is arranged approximately in the order of the magnitude of distortion so that any connection between this and the character of the molecular structure may be readily seen. Or, expressed in another way, one might hope the results to indicate the detailed character of the chain. For example, do the results indicate that the normal chain is a spiral with the lines joining centers of the carbon atoms having an angle of 109°28′, and with the spiral completed by a fourth atom? The results do not give an answer. One reason is that the distortion may be too great to betray the detail of the normal chain. Another is that we may be pushing the results further than the purity of the compounds warrant. At any rate, while there is no definite answer reached as to detailed structure, the results are not inconsistent with the assumption of distortion.

The results give evidence either for distortion with all the isomers or for a closer packing. But the differences from 25.4 to 2.7 percent can scarcely be accounted for by differences in packing, and distortion is proved in either event. This distortion would probably consist not only of bending but of alterations in the separation of the carbon atoms. The distortion also accounts for the similarity in change in diameter and the difference shown by comparison with alcohol isomers, both of which were mentioned under (1) above.

(3) *3 Ethyl pentane.* This molecule is a symmetrically branched chain. It can scarcely be classed with the other heptanes in the preceding discussion on distortion.

Table I shows that its increase in diameter is only 0.87A. This may be accounted for by a symmetrically branched chain with the three branches in the same plane and forming angles of 60° with each other. But one might expect that two diameters would be shown instead of one. Doubtless the lack of uniformity in the groups is the explanation.

Assuming the same structure, and making a reasonable allowance for the central carbon atom, the value of L_2 becomes 8.30A. L_1 as computed by Eq. (1) is 7.84A. The distortion as measured by $(L_2-L_1)/L_2$ is only 5.5 percent.

(4) *2 methyl hexane, and 2 methyl hexylene 2.* The 2 methyl hexane gives two diameters. This is the second case in the work of this laboratory when the resolving power of the liquid groups was sufficient to give two diffraction peaks for an isomer. The other case is that of di-n-propyl carbinol. Using one of these peaks, $(L_2-L_1)/L_2$ gives -3.1 percent and with the other it is $+12.5$ percent. If, instead of this procedure, the product of the two diameters be used in measuring L_1 its value would be 9.63A. If it is assumed that five of the carbon atoms are in a "straight" chain, that the length of the fifth molecule along the chain belongs half to the straight portion and half to one of the branches, and if the angle between the branches is 60°, then the length L_2, computed by Eq. (2), is 9.61A. L_2 and L_1 are essentially equal. This seems to give evidence that the only distortion in the chain is the branching of the CH_3 groups from the last carbon atom.

(5) *Effect of point of attachment of branches.* The increase in diameter with the two CH_3 groups attached either to adjacent or non-adjacent carbon atoms seems to alter the diameter by the same amount, 1.04A. This is shown by the 3-3, 2-2, 2-3 and 2-4 dimethyl pentanes.

The attachment of the two CH_3 groups to the same atom may or may not increase the diameter by the same amount, 1.04, this depending upon whether a third CH_3 branch is attached to an adjacent atom (2-2-3 trimethyl butane) or a non-adjacent one (2-2-4 trimethyl pentane). Inasmuch as only one comparison is made, the conclusion is highly tentative.

The attachment of a CH_3 group on the next to the end C atom may alter the end of the chain causing a symmetrical arrangement of the two CH_3 groups and increasing the diameter of the molecule by a relatively small amount. This is illustrated by 2 methyl hexylene 2 and 2 methyl hexane. They both have an increase of diameter of about 0.2A as compared with an increase in the alcohol chains of 0.5A for a CH_3 branch.

These experiments suggest the possibility of reaching fairly definite conclusions as to the detailed nature of the paraffin chains. This would require experiments on a large number of isomers of the normal paraffins.

(6) *Comparison of the chains of the normal primary alcohols, saturated fatty acids and paraffins.* In connection with the foregoing discussion on the distortion of the straight chain in the case of an isomer, it is appropriate to refer to the data for the dependence of diameter upon the carbon content in the cases of the three normal series thus far tested in this laboratory. These data are found in the articles by Stewart and Morrow, Morrow and Stewart to which reference has already been made. The variation in diameter with primary normal alcohols varies linearly from eleven carbon atoms to three, the total variation being from 4.5A to 4.3A. From three carbon atoms to one, a rapidly increasing change sets in. The chains of the saturated normal fatty acids are, on the contrary, quite constant in diameter from eleven carbon atoms to four, and from four to one carbon atom its rapid decrease agrees, as nearly as can be determined, with the case of the alcohols. The normal paraffins have a diameter of 4.64A which is constant from fifteen to five carbon atoms content. The three do not appear to have like diameters

at any length except with less than four carbon atoms. Moreover the alcohols vary linearly while the paraffins and acids remain constant. This strengthens the view that the detailed nature of the chain, both as to diameter and longitudinal separation of carbons, depends upon the terminal groups.

There is also evidence that the isomers of primary normal alcohols do not have the amount of distortion found in the paraffin isomers. This can be shown by the comparisons of the measured lengths with those computed by a formula similar to Eq. (2). If it is assumed that the longitudinal separation of carbon atoms in the primary normal alcohols is the same as in normal paraffins, i.e., 1.24Å, then a consideration of the primary normal alcohol data shows that the atom of oxygen occupies the same longitudinal length as the carbon atom. Then Eq. (2) may be used provided n refers to O as well as to C. Computations with Eq. (2) may then be made of the lengths of the molecule of the alcohol isomers and compared with the projections of the lengths taken normal to the planes. When this is done, and double molecules are assumed, the angle of projection does not vary more than a few degrees, i.e., from 40° to 45°, with the exception of diethyl carbinol, di-n-propyl carbinol and tertiary amyl. With the first and second the angle becomes approximately zero, if single molecules are assumed. They are the only ones in which OH is a branch attached not to a carbon adjacent to the terminal atom. If this be the correct interpretation then the alcohol chain seems more fixed than the paraffin chains, even with the OH group in a branch, both because of the lack of a wide divergence in angle and because of the agreement of computations and measurements in the two cases cited. Tertiary amyl gives a considerable divergence of angle, approximately 10° less than that cited above.

General Conclusions

Stated in a broad way the conclusions are that the paraffin carbon chains are distorted by branch groups, that the normal paraffin chains have the same diameter irrespective of length if containing more than five atoms, that the x-ray diffraction method in liquids seems to promise a considerable amount of knowledge concerning the structure of carbon chains, and that as evidence accumulates it increasingly favors the interpretation of the author as to the cybotactic state in liquids and the recognition of its importance in all fundamental liquid phenomena.

The author desires to express his appreciation of the assistance of the Ethyl Gasoline Corporation through Dr. Graham Edgar and Dr. George Calingaert, and of Mr. H. A. Zahl, research assistant, who has taken the observations herein reported.

Physics Laboratory,
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May 18, 1928.

THEORY OF THE DOUBLE X-RAY SPECTROMETER

By M. M. Schwarzschild

Abstract

The geometric factors in the construction and use of the double x-ray spectrometer are examined in detail. It is found that the resolution of the instrument is not affected by the width of the slits but that, on the other hand, the height of the slits must be limited to preserve resolution. A formula is given for the limiting value of the ratio—average height of effective slits: distance between effective slits—for any particular width of observed line, in order that the width observed be the result principally of the physical factors. The physical factors, namely, crystal imperfection, line width, diffuseness of absorption limits, are also discussed and formulas are derived by means of which the experimental curves found with the instrument may be interpreted physically.

IN RECENT work of Bergen Davis, Slack and Purks on various problems involving a high resolution in the x-ray region they have made use of the double x-ray spectrometer. The instrument is essentially an ordinary spectrometer with the addition of a second crystal which may be turned through accurately measured small angular intervals. It is described in sufficient detail in the papers of Davis and Slack[1] and Davis and Purks.[2,3] The arrangement had been used by Davis and Stempel[4] in their classic measurement of the efficiency of reflection of crystals. Ehrenberg and Mark[5] have also used this arrangement for work similar to that of Davis and Purks.

The present paper is the result of an attempt to determine theoretically the various factors which should be taken into account in the use of the instrument, and to deduce the relations which exist between the characteristics of the radiation entering the instrument, the perfection of the crystals, and the curves found experimentally by means of the instrument. It may be considered as an extension of the work of Richtmyer,[8] since it attempts to develop for the double spectrometer relations similar to those he developed (graphically) for the single crystal instrument.

This discussion is divided into three parts. Part I deals with the effect of poor adjustment of the crystals as to verticality and with the effect of finite slit dimensions. The argument in this part is based upon the assumption of geometrically ideal Bragg reflectors. The results of Part I are therefore not directly applicable to the real situation. Part II is a discussion of the effects of real crystals and real radiation. Relations are found for various types of entering radiation connecting the form of the observed curves with the actual wave-length distribution. In Part III the condition which the slit heights must fulfill in order that the results of Part II may be applied is given. The application of those results to the work of Davis and Purks is then discussed.

I. Geometrical

We set ourselves the problem of finding the relations which must be satisfied by the directional coordinates of an incoming ray of wave-

length λ in order that it may be reflected from both crystals. The geometric situation is rather complicated and it seems simpler to derive a vector equation first, and then to translate it into angular notation.

In Fig. 1 AB and CD are the traces on the xy or horizontal plane of two idealized Bragg reflectors mounted so that by rotating the supports of either or both, the angle β between these traces may be varied. The vector $\boldsymbol{r}$ is a unit vector in the direction of the incoming ray, the vector $\boldsymbol{R}$ is a unit vector in the direction of this ray after the first reflection. The vectors $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are the unit normals drawn out from the two reflecting surfaces. In the figure only the projections of these vectors on the xy plane are shown. The angles indicated in the figure are angles between horizontal traces and projections only. The x axis makes the angle θ_1 with AB and the line EF makes the angle θ_2 with CD. These angles are the Bragg angles for the reflection under consideration. The angle ω is the angle between the horizontal projection of $\boldsymbol{r}$ and the x axis. The angle ϵ is the angle between the horizontal projection of $\boldsymbol{R}$ and EF. Angles not shown in the figure but readily visualized are: the angle ψ between $\boldsymbol{r}$ and its horizontal projection, the angle δ_1 between $\boldsymbol{n}_1$ and its horizontal projection, and the angle δ_2 between $\boldsymbol{n}_2$ and its horizontal projection. The z axis is to be considered as coming out of the plane of the figure.

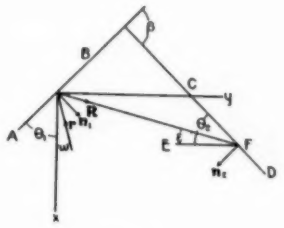

Fig. 1.

The conditions for reflection of the incoming ray from the first crystal may be written

$$\boldsymbol{r}\cdot\boldsymbol{n}_1 = -\sin\theta_1 = -p_1\lambda/2d\ ;\ \boldsymbol{r}\cdot\boldsymbol{n}_1 = -\boldsymbol{R}\cdot\boldsymbol{n}_1\ ;\ \boldsymbol{r}\times\boldsymbol{n}_1 = \boldsymbol{R}\times\boldsymbol{n}_1. \quad (1)(2)(3)$$

where p_1 is the order of the first reflection and d the crystal lattice constant. In order that the ray reflected from the first crystal be again reflected from the second, at order p_2, we must have

$$\boldsymbol{R}\cdot\boldsymbol{n}_2 = -\sin\theta_2 = -p_2\lambda/2d = p_2\boldsymbol{r}\cdot\boldsymbol{n}_1/p_1 \quad (4)$$

By operating upon both members of Eq. (3) with $\boldsymbol{n}_1\times$, expanding the triple product and substituting from Eq. (2), we obtain

$$\boldsymbol{R} = \boldsymbol{r} - 2\boldsymbol{r}\cdot\boldsymbol{n}_1\boldsymbol{n}_1 \quad (5)$$

By operating upon both members of Eq. (5) with $\boldsymbol{n}_2\cdot$, and using Eq. (4) we derive

$$p_1\boldsymbol{r}\cdot\boldsymbol{n}_2 - 2p_1\boldsymbol{r}\cdot\boldsymbol{n}_1\boldsymbol{n}_1\cdot\boldsymbol{n}_2 = p_2\boldsymbol{r}\cdot\boldsymbol{n}_1 \quad (6)$$

an equation which with Eq. (1) expresses the condition for the double reflection of the incoming ray.

In order that these equations may be of further use it is necessary that they be rewritten in terms of the direction coordinates of the vectors involved. The following equations are easily seen to be a consequence of our definitions of the angles involved, with the added consideration that all powers of δ_1 and δ_2 above the first are neglected.

$$\begin{aligned} r_x &= -\cos\psi\cos\omega & n_{1x} &= \sin\theta_1 & n_{2x} &= \sin(\theta_1+\beta) \\ r_y &= -\cos\psi\sin\omega & n_{1y} &= \cos\theta_1 & n_{2y} &= \cos(\theta_1+\beta) \\ r_z &= -\sin\psi & n_{1z} &= \delta_1 & n_{2z} &= \delta_2 \end{aligned} \tag{7}$$

With the help of Eqs. (7), we may write Eq. (6) in trigonometric form. Noting Eq. (1) we get

$$p_1\cos\psi\sin(\omega+\theta_1+\beta)+p_1\delta_2\sin\psi-2p_1\sin\theta_1\cos\beta=p_2\sin\theta_1 \tag{8}$$

Eq. (1) may be written in angular notation as

$$\cos\psi\sin(\omega+\theta_1)=\sin\theta_1-\delta_1\sin\psi \tag{9}$$

or

$$\cos\psi\cos(\omega+\theta_1)=(\cos^2\psi+2\delta_1\sin\theta_1\sin\psi-\sin^2\theta_1)^{1/2} \tag{10}$$

Noting the identity

$$\sin(\omega+\theta_1+\beta)=\sin\beta\cos(\omega+\theta_1)+\cos\beta\sin(\omega+\theta_1)$$

we may substitute from Eqs. (9) and (10) in Eq. (8) and get

$$\sin\beta(\cos^2\psi+2\delta_1\sin\theta_1\sin\psi-\sin^2\theta_1)^{1/2}-\cos\beta(\sin\theta_1+\delta_1\sin\psi)=\sin\theta_2-\delta_2\sin\psi \tag{11}$$

Introduce the angles γ and η such that

$$\sin\beta\cos\gamma-\cos\beta\sin\gamma=\sin\eta \tag{12}$$

Comparing Eqs. (11) and (12) and neglecting terms in ψ of degree above the second, as well as those in δ higher than the first, we have

$$\gamma=\sin^{-1}(\sin\theta_1+\delta_1\psi-2\sin^2\theta_1\delta_1\psi+\tfrac{1}{2}\sin\theta_1\psi^2) \tag{13}$$

$$\eta=\sin^{-1}(\sin\theta_2-\delta_2\psi-2\sin\theta_1\sin\theta_2\delta_1\psi+\tfrac{1}{2}\sin\theta_2\psi^2) \tag{14}$$

Expanding arcsin by Taylor's theorem about $\sin\theta_1$ and $\sin\theta_2$ respectively, we obtain

$$\gamma=\theta_1+\delta_1\psi/\cos\theta_1-2\sin\theta_1\tan\theta_1\delta_1\psi+\tfrac{1}{2}\tan\theta_1\psi^2 \tag{15}$$

$$\eta=\theta_2-\delta_2\psi/\cos\theta_2-2\sin\theta_1\tan\theta_2\delta_1\psi+\tfrac{1}{2}\tan\theta_2\psi^2\ [1] \tag{16}$$

Evidently, from Eq. (12) $\sin(\beta-\gamma)=\sin\eta$, which yields the two solutions

$$\beta-\eta-\gamma=0 \quad : \quad \beta-\pi+\eta-\gamma=0 \tag{17)(18}$$

These solutions may be written, using Eqs. (15) and (16),

$$M\psi^2+R\psi=\Delta \tag{19}$$

where $\Delta=\beta-[\theta_1+\pi/2\pm(\theta_2-\pi/2)]$ representing the angular deviation of the position of the second crystal from the position for reflection of a horizontal ray of wave-length λ entering along the x axis, $R=\delta_1/\cos\theta_1+\delta_2/\cos\theta_2-$

[1] These series will not be convergent even for small values of ψ if the orders of reflection are so great that the functions of the θ's entering in the ψ and δ terms are very large. For orders used in practice this restriction is unimportant.

$2 \sin \theta_1(\tan \theta_1 \pm \tan \theta_2)\delta_1$ or, by an obvious approximation $R=\delta_1+\delta_2$[2] representing the sum or difference of the angles of inclination of the crystals to the vertical, and $M=\frac{1}{2}(\tan \theta_1 \pm \tan \theta_2)$, the upper signs being taken when the crystals are in the position of Case I, Fig. 2, in which the ray incident on the first crystal and the ray reflected from the second crystal lie on the same side of the ray reflected from the first crystal; the lower signs being taken when the crystals are in the position of Case II, Fig. 2, in which the first incident and the last reflected rays are on opposite sides of the first reflected ray.

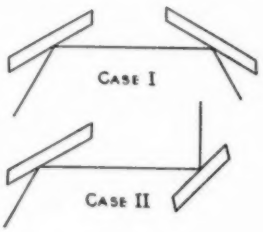

Fig. 2.

The angle Δ which determines the position of the second crystal is thus seen to be independent of ω,[3] the angle whose limits are fixed by the horizontal width of the slits, but does depend upon ψ, the angle whose limits are fixed by s, the average vertical height of the effective slits and L, the distance between the effective slits. Evidently

$$-s/L<\psi<s/L \tag{20}$$

We now proceed to find the relation between the angle Δ and the energy reflected by the second crystal. We may suppose that the energy coming through the slits at the angle ψ is a function of that angle. If we denote by $I(\psi)$ a quantity proportional to the energy of the beam making the angle ψ with the horizontal plane, then, whatever the form of this function,

$$I(\psi)=0 \text{ for } |\psi| \geqq s/L. \tag{21}$$

Eq. (19) has two solutions for every value of Δ. We denote these values of ψ by ψ_1 and ψ_2. If I_Δ is proportional to the energy coming through after the second reflection, we may write

$$I_\Delta=I(\psi_1)+I(\psi_2), \tag{22}$$

In Fig. 3a the parabolas are the graphs of Eq. (19) for various values of R. Fig. 3b gives the corresponding curves relating I_Δ and Δ if $I(\psi)=s/L-|\psi|$ for $|\psi|<s/L$, physically realized if the effective slits are equal in height and the source uniform. If the effective slits differ very much in height, then for $|\psi|<s/L$, $I(\psi)=$constant. The relations between I_Δ and Δ are obvious from Eq. (22). The curves of Fig. 3a are drawn on the assumption that both R and M are positive. If R were negative the effect would be merely to invert the scale of ψ, i.e., make it positive downward. Since in ordinary cases $I(\psi)$ depends only on the absolute value of ψ, the distribution would be unchanged. If M were negative the effect would be an inversion of the

[2] There is no pretense at accuracy in this equation. It merely serves to give a rough interpretation of R. For the further argument all we need say is that R is not a function of ψ or ω and may be made as small as we please by proper choice of δ_1 and δ_2.

[3] Except that ω must be so limited that $\omega+\theta_1<\pi/2$. Practically, for orders of reflection used in practice, this condition is automatically fulfilled because of limitation of crystal size. The reason for this condition lies in the selection of signs in Eqs. (9) and (10).

scale of Δ, i.e., positive to the left. The distributions would thus simply be reversed in Δ.

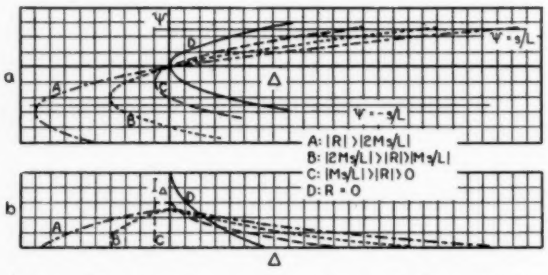

Fig. 3. (a) Graph of Eq. (19) for various values of R. ψ is the ordinate, Δ the abscissa. (b) Corresponding curves relating I_Δ and Δ.

A consideration of the geometry of the curves of Fig. 3a shows that the maximum width of the curves for I_Δ may be expressed by the relations

$$W = 2Rs/L \text{ for } R > 2Ms/L \tag{23}$$

and

$$W = Ms^2/L^2 + Rs/L + R^2/4M \text{ for } R < 2Ms/L$$

where R and M are always to be taken positively. These equations may be transformed into more practical units. If R' denotes the value of R expressed in minutes of arc, and W'' denotes the value of W expressed in seconds of arc, we have, approximately

$$\begin{aligned} W'' &= 120R's/L \text{ for } R' > 7\cdot 10^3 Ms/L \\ W'' &= 2\cdot 10^5 Ms^2/L^2 + 60R's/L + 4\cdot 10^3 R'^2/M \text{ for } R' < 7\cdot 10^3 Ms/L \end{aligned} \tag{24}$$

R' and M again being taken positively.

Fig. 4 shows the graph of W'' and R' for various values of s/L and M. It is obvious from the figure that the most accurate adjustment of R', which

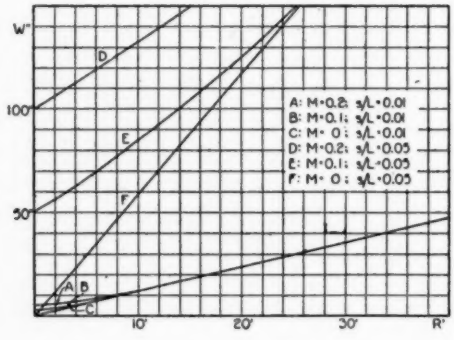

Fig. 4. The geometric width as a function of R, the deviations from true verticality.

determines the verticality of the crystals, may be made by adjusting R' for the narrowest curves, when s/L is large. Furthermore, for $M \neq 0$, the value of W remains greater than zero for all values of R. The quantity W'' represents only the width due to "geometric" causes. We have assumed that our

crystals are ideal Bragg reflectors and, at least in the non-parallel case, that the radiation is ideally monochromatic. Actually, of course, this is not the case. In fact, the minimum observed widths are all considerably larger than the value of W'' for $R=0$, and reasonable values of M and s/L. The widths of the observed curves, when adjusted, is therefore principally due to the "physical" causes enumerated above. We may, for this reason, in our discussion of physical causes neglect the geometric width, as soon as R' and s/L are properly adjusted. This may be done readily. For a given value of M it is only necessary to make s/L large and adjust R' for minimum width of observed line. The observed width will then be largely "geometrical." If, now, s/L is decreased so that the value of W'' from Eq. (24) for $R'=0$ is small compared to the observed width at that setting, our instrument is in such adjustment that the line width observed is principally due to "physical" causes.

It is important to note that, because of the change of sign in the definition of R, between Case I and Case II, an adjustment for verticality in one case cannot be relied upon for the other, no matter how accurately the crystal mountings are designed.

II. Physical

The results of the last section show that the width of the observed lines which may be ascribed to the geometric arrangement of the system may, under reasonable conditions, be made very small. Under the best experimental conditions, however, the actual observed widths are much greater. Their source lies in the fact that we are dealing with real crystals and with radiation of finite wave-length range.

Consider the case in which the rays are ideally monochromatic, but the crystals real. Giving ω the same meaning as in Part I, Fig. 1, we may set the energy of the beam after reflection from the first crystal as proportional to $A_1 e^{-k_1\omega^2}$, if θ_1 of Fig. 1 is the Bragg angle corrected for refraction of the wave-length in question. The justification of this relation rests upon the following:

1. For a perfect crystal the distribution predicted by Ewald and Darwin is shown by the solid line in Fig. 5. The distribution we assume may, by proper choice of A and k, be made to fit this reasonably well as shown by the dotted curve in Fig. 5.

2. For an imperfect crystal reflection must be considered as coming from a large number of microcrystals arranged about a mean position. The Guassian probability function is the most likely distribution.

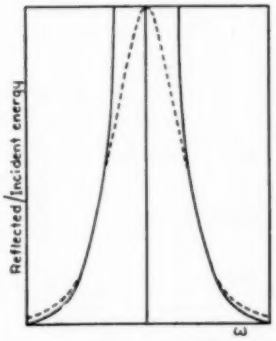

Fig. 5.

If θ_2 is the corrected Bragg angle for the second reflection, and ϵ has the meaning for the second reflection which ω has for the first, we have, from Eqs. (17) and (18)

for Case I ; $$\theta_2-\epsilon=\beta-\theta_1-\omega \tag{25}$$

for Case II : $$\theta_2-\epsilon=\beta-\pi-\theta_1-\omega \tag{26}$$

ω and ϵ here represent the deviations of the actual reflected ray from the position of the ray reflected by an ideal Bragg reflector.

$A_2e^{-k_2\epsilon^2}$ represents a function of ϵ proportional to the fraction of the incident energy reflected by the second crystal. The ratio of the total energy getting through both crystals, to that incident on the first will be the product of the corresponding ratios for each crystal, i.e.,

$$F=A_1A_2e^{-(k_1\omega^2+k_2\epsilon^2)} \tag{27}$$

If we denote by α the position of the second crystal as measured from its ideal position, we have

for Case I : $$\alpha=\beta-\theta_1-\theta_2 \tag{28}$$

for Case II : $$\alpha=\beta-\pi-\theta_1+\theta_2 \tag{29}$$

Combining the last five equations we obtain

$$F=A_1A_2e^{-[k_1\omega^2+k_2(\alpha-\omega)^2]} \tag{30}$$

and, since ω has a wide range, the total energy coming through at α will be proportional to

$$J=\int_{-\infty}^{+\infty}Fd\omega \tag{31}$$

Integrals of this type may be evaluated as follows:

$$\int_{-\infty}^{+\infty}e^{-[ax^2+b(y-cx)^2]}dx=[\pi/(bc^2+a)]^{1/2}e^{-abc^2/(bc^2+a)} \tag{32}$$

so that

$$J=A_1A_2[\pi/(k_1+k_2)]^{1/2}e^{-k_1k_2\alpha^2/(k_1+k_2)} \tag{33}$$

For parallel crystals $\theta_1=\theta_2$ and hence by Eq. (29) α is independent of the wave-length. Under any other conditions α depends on θ_1 and θ_2 and hence upon the wave-length. Suppose that the radiation entering the spectrometer be polychromatic, and that the distribution of energy with the wave-length be described by a function $f(\lambda-\lambda_0)$ where λ_0 is a unique wave-length peculiar to the distribution (center of line, absorption edge, etc.). The energy coming through at any position of the second crystal is evidently proportional to

$$A_1A_2[\pi/(k_1+k_2)]^{1/2}\int_{-\infty}^{+\infty}f(\lambda-\lambda_0)e^{-k_1k_2\alpha^2/(k_1+k_2)}d\lambda \tag{34}$$

By definition, Eqs. (28) and (29), α is the deviation of the position of the second crystal from the ideal position for the wave-length considered. If α_c represents the same deviation as measured from the ideal position for λ_0

$$\alpha=\alpha_c-(\lambda-\lambda_0)d(\theta_1\pm\theta)/d\lambda \tag{35}$$

the upper sign being taken for Case I, and the lower for Case II. Denoting $k_1k_2/(k_1+k_2)$ by K_c and $d(\theta_1+\theta_2)/d\lambda$ by r the expression (34) becomes

$$A_1A_2\pi^{1/2}/r(k_1+k_2)^{1/2}\int_{-\infty}^{+\infty}f[(\alpha_c-\alpha)/r]e^{-K_c\alpha^2}d\alpha \tag{36}$$

For the case of line radiation we may assume

$$f(\lambda-\lambda_0)=Ee^{-K_\lambda(\lambda-\lambda_0)^2} \tag{37}$$

Substituting in Eq. (36) and using Eq. (32), we obtain

$$J_{\alpha_c}=\frac{\pi EA_1A_2}{[(K_cr^2+K_\lambda)(k_1+k_2)]^{1/2}}e^{-K_cK_\lambda\alpha_c^2/(K_\lambda+K_cr^2)} \tag{38}$$

For the case of continuous radiation we have, for the small ranges under consideration $f(\lambda-\lambda_0)=C$. For this case Eq. (36) becomes

$$J_{\alpha_c}=CA_1A_2\pi/r[K_c(k_1+k_2)]^{1/2} \tag{39}$$

For the case of an absorption edge we may set

$$f(\lambda-\lambda_0)=B+(1/h_a)\int_{-\infty}^{\lambda-\lambda_0}(A-B)e^{-\pi x^2/h_a^2}dx \tag{40}$$

A graph of this equation is shown in Fig. 6. The quantity h_a has the significance shown in the figure, and may be used as a measure of the diffuseness of the absorption edge. In this case Eq. (36) becomes

$$J_{\alpha_c}=\frac{A_1A_2\pi^{1/2}}{r(k_1+k_2)^{1/2}}\left[\int_{-\infty}^{+\infty}Be^{-K_c\alpha^2}d\alpha+\frac{1}{h_a}\int_{-\infty}^{+\infty}e^{-K_c\alpha^2}\int_{-\infty}^{(\alpha_c-\alpha)/r}(A-B)e^{-\pi x^2/r^2h_a^2}dxd\alpha\right]$$

so that

$$\frac{dJ_\alpha}{d\alpha_c}=\frac{A_1A_2\pi^{1/2}(A-B)}{r^2h_a(k_1+k_2)^{1/2}}\int_{-\infty}^{+\infty}e^{-[K_c\alpha^2+\pi(\alpha-\alpha_c)^2/r^2h_a^2]}d\alpha$$

and, by Eq. (32)

$$\frac{dJ_{\alpha c}}{d\alpha_c}=\frac{A_1A_2\pi(A-B)}{r[(\pi+K_cr^2h_a^2)(k_1+k_2)]^{1/2}}e^{-\pi K_c\alpha_c^2/(\pi+K_cr^2h_a^2)}$$

giving

$$\left(\frac{dJ_{\alpha_c}}{d\alpha_c}\right)_{\alpha_c=\alpha}=\frac{A_1A_2\pi(A-B)}{r[(\pi+K_cr^2h_a^2)(k_1+k_2)]^{1/2}} \tag{41}$$

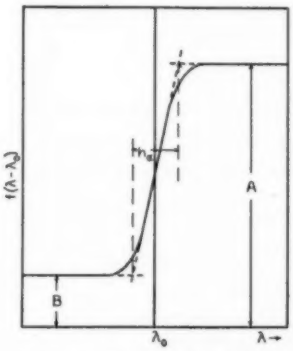

Fig. 6. Graph of Eq. (40).

From Eq. (39) it is evident that the ordinates of the observed curve far on either side of the absorption edge will be $AA_1A_2\pi/r[K_c(k_1+k_2)]^{1/2}$ and $BA_1A_2\pi/r[K_c(k_1+k_2)]^{1/2}$, so that the observed angular width will be

$$h=\frac{(A-B)\pi A_1 A_2}{r[K_c(k_1+k_2)]^{1/2}}\div\left(\frac{dJ_{\alpha_c}}{d\alpha_c}\right)_{\alpha_c=\alpha}$$

Using Eq. (41) this becomes

$$h=(\pi/K_c+r^2h_a^2)^{1/2}$$

For the probability distributions of Eqs. (30), (33), (37), and (38) we may use as a measure of the width, that at half-maximum energy, which may be expressed as $2(\log 2)^{1/2}/K^{1/2}$ where K is the constant of the exponent. If H_1 and H_2 represent these widths for each of the crystals for ideally collimated and monochromatic radiation, we have, using appropriate subscripts, from Eq. (33)

$$H_c=(H_1^2+H_2^2)^{1/2} \tag{43}$$

or, if the crystals are alike

$$H_c=\sqrt{2}H_1 \tag{44}$$

If the crystals are not parallel the observed angular width $H_{n.p.}$ for a line will be, from Eqs. (37) and (38)

$$H_{np}=(H_c^2+r^2H_\lambda^2)^{1/2} \tag{45}$$

If the crystals are parallel, the observed angular width H_p will be

$$H_p=H_c \tag{46}$$

evidently independent of the type of radiation. From Eqs. (42), (43), and (46), the actual width h_a of an absorption edge, in wave-length units is related to the observed angular width h and the resultant width for the two crystals at the orders used, H_c, in the following manner:

$$r^2h_a^2=h^2-\pi H_c^2/4\log 2=h^2-1.13H_c^2 \tag{47}$$

The quantity r in the above equations may be expressed as

$$r=d(\theta_1\pm\theta_2)/d\lambda=p_1/2d\cos\theta_1\pm p_2/2d\cos\theta_2 \tag{48}$$

The results expressed by Eqs. (43) to (46) have already been published by Ehrenberg and Mark[5] for the case $\theta_1=\theta_2$. The results here are more general and may be applied even to the case of two crystals of different material.

III. Application

The results of Part II may be applied only if the "geometric" width given by Eq. (23) is small compared to the measured widths, H_p, $H_{n.p.}$, or h. This limitation may be expressed in the following way:

$$\frac{s}{L}\ll\left(\frac{\text{angular width measured}}{\frac{1}{2}(\tan\theta_1\pm\tan\theta_2)}\right)^{1/2}$$

the upper sign being taken for case I, and the lower for case II. It is, of course, assumed that the adjustment for verticality has been taken care of.

In all the work of Davis and Purks[3] this limitation has been taken into consideration. These authors have recently shown[3] that the natural width of the $K\alpha$ line of Mo is of the order of 0.1 X-unit. In that work they made use of the equation of Ehrenberg and Mark[5] corresponding to our Eq. (45).

It is of interest to apply Eq. (44) to the data there given. They found with both crystals parallel and reflection at second order $H_2 = 3.75''$, which gives $H_1 = 2.65''$. The corresponding quantity at first order would be twice as great[6] or $5.4''$ which is to be compared with the value $5.8''$ given by Compton[7] for a perfect crystal. The result indicates a high order of perfection for the calcite crystals used. If we adopt the value for H_1 at first order as $5.4''$ we can calculate the breadth of an absorption edge from unpublished data of Davis and Purks. They find for the Mo K limit $h = 32'' = 1.6 \times 10^{-4}$ radians at first order on both crystals of calcite, reflecting as in case I. From Eq. (48) $r = 0.33$ (A-units)$^{-1}$, from Eq. (44) $H_c = 7.5'' = 3.7 \times 10^{-5}$ radians, and hence, from Eq. (47), $h_a = 4.65 \times 10^{-4}$ A-units.

This result is to be compared with the upper limit for the width of the Ag K absorption edge given by Richtmyer[8] as 0.0002 A-units.

COLUMBIA UNIVERSITY,
March 26, 1928.

[1] Davis and Slack, Phys. Rev. **27**, 18 (1926).
[2] Davis and Purks, Proc. Nat. Acad. Sci. **13**, 419 (1927).
[3] Davis and Purks, Proc. Nat. Acad. Sci. **14**, 172 (1928).
[4] Davis and Stempel, Phys. Rev. **17**, 608 (1921).
[5] Ehrenberg and Mark, Zeits. f. Physik **42**, (1927).
[6] C. G. Darwin, Phil. Mag. **27**, 675 (1914).
[7] A. H. Compton, X-rays and Electrons, p. 140.
[8] F. K. Richtmeyer, Phys. Rev. **26**, 724 (1925).

THE SPECTRUM OF SULPHUR, S II

By S. B. Ingram

Abstract

One hundred and eighty-three lines are classified in the spectrum of S II. Thirty-three terms of the quartet system and thirty-six of the doublet system are determined and correlated with the electron configurations by means of the Hund theory. The *ionization potential* of the S II ion is fixed at 23.3 ± 0.1 volts.

Experimental Work

THE sulphur spectrum above 2000A was obtained by passing a condensed discharge through H_2S gas. At higher pressures the Balmers eries predominated but as the pressure was reduced towards the limiting value at which a discharge could sustain itself the hydrogen lines became relatively weak and the sulphur spectrum came out with great intensity. When the self induction of the discharge circuit was reduced to a minimum the lines of S II, III, IV and V appeared strongly on the plates. Insertion of sufficient self induction into the circuit to reduce the frequency of oscillation, and hence the instantaneous value of the current, to about one-tenth its former value completely suppressed all these except the S II lines. The visible and ordinary ultra-violet regions were photographed by means of a 7 meter concave grating in a Rowland mounting. In the ultra-violet these observations were supplemented by a plate taken on a Hilger quartz spectrograph E2. In the extreme ultra-violet the spectrum of a hot spark was photographed on a vacuum spectrograph with a grating of one meter radius. The exactness with which the data fit the series relationships gives a check on the accuracy of the measurements. The probable errors, estimated in this way are: for

Table I. *Predicted terms of S II.*

Electron configuration		Prefix	Terms	Prefix	Terms	Prefix	Terms
	s^2p^3	a	^4S				
		a	$^2D\,^2P$				
	sp^4	b	^4P				
		b	$^2P\,^2D\,^2S$				
S III ion	s^2p^2		^3P		^1D		^1S
S II	$s^2p^2 \cdot ms$	ms	^4P				
		ms	^2P	ms'	^2D	ms''	^2S
	$s^2p^2 \cdot mp$	mp	$^4S\,^4P\,^4D$				
		mp	$^2S\,^2P\,^2D$	mp'	$^2P\,^2D\,^2F$	mp''	^2P
	$s^2p^2 \cdot md$	md	$^4P\,^4D\,^4F$				
		md	$^2P\,^2D\,^2F$	md'	$^2S\,^2P\,^2D\,^2F\,^2G$	md''	^2D
	$s^2p^2 \cdot mf$	mf	$^4D\,^4F\,^4G$				
		mf	$^2D\,^2F\,^2G$	mf'	$^2P\,^2D\,^2F\,^2G\,^2H$	mf''	^2F

the measurements on the large grating about 0.02A, on the quartz spectrograph about 0.3A, and on the vacuum spectrograph about 0.03A. Some of the weaker lines have been taken from old data appearing in Kayser's Handbuch der Spectroscopie. The probable error in these measurements appears to be about 0.2A.

Predicted Terms

The spectrum of sulphur II should be similar to that of oxygen II containing a doublet and quartet system. Table I gives a summary of the predictions of the Hund theory. The notation used is standard excepting for the introduction of primes on the letter referring to the orbit of the excited electron. Unprimed terms are based on the ^3P state of the S III ion, singly primed terms on the ^1D state and doubly primed terms on the ^1S state. Those terms which have been observed are in bold face in the table.

Term Values

Two members of both the series of terms ms^4P and ms^2P, $m=4$, 5, have been detected, thus making possible the determination of the term values and of the ionization potential. In fixing the terms $4s^4P$, and $4s^2P$, an increase of effective quantum number of 1.02 between the terms $4P$ and $5P$ has been assumed. This assumption is arbitrary except insofar as it is justified by analogy with the terms of O II and of other light elements. The term values calculated on this assumption are about 700 cm^{-1} less than those determined by an ordinary Rydberg formula. The combination of the $4s^4P$ term with the low ^4S term in the extreme ultra-violet fixes the ground term of the S II ion at 188824.5 cm^{-1} giving an ionization potential of 23.3 ± 0.1 volts. The complete list of term values is given in Table II. Since no intercombinations

Table II. *Term values.*

			s^2p^2		
$a^4S_{\frac{3}{2}}$	188824.5	$a^2P_{\frac{3}{2}}$	163934.5	$a^2D_{\frac{5}{2}}$	173623.9
		$a^2P_{\frac{1}{2}}$	163983.1	$a^2D_{\frac{3}{2}}$	173655.4
			sp^4		
$b^4P_{\frac{5}{2}}$	109429.7	$b^2P_{\frac{3}{2}}$	82908.36		
$b^4P_{\frac{3}{2}}$	109066.6	$b^2P_{\frac{1}{2}}$	82463.28		
$b^4P_{\frac{1}{2}}$	108856.5				
Terms based on S III ^3P				Terms based on S III ^1D	
			$s^2p^2 \cdot 4s$		
$4s^4P_{\frac{5}{2}}$	78556.17	$4s^2P_{\frac{3}{2}}$	75045.88	$4s'^2D_{\frac{5}{2}}$	66977.31
$4s^4P_{\frac{3}{2}}$	78993.17	$4s^2P_{\frac{1}{2}}$	75570.00	$4s'^2D_{\frac{3}{2}}$	66978.87
$4s^4P_{\frac{1}{2}}$	79264.00				
			$s^2p^2 \cdot 5s$		
$5s^4P_{\frac{5}{2}}$	37828.16	$5s^2P_{\frac{3}{2}}$	36596.42		
$5s^4P_{\frac{3}{2}}$	38293.29	$5s^2P_{\frac{1}{2}}$	37123.21		
$5s^4P_{\frac{1}{2}}$	38566.02				
			$s^2p^2 \cdot 4p$		
$4p^4S_{\frac{3}{2}}$	57795.79			$4p'^2P_{\frac{3}{2}}$	44883.79
				$4p'^2P_{\frac{1}{2}}$	45018.43
$4p^4P_{\frac{5}{2}}$	58690.48	$4p^2P_{\frac{3}{2}}$	55107.43		
$4p^4P_{\frac{3}{2}}$	58966.43	$4p^2P_{\frac{1}{2}}$	55238.70	$4p'^2D_{\frac{5}{2}}$	47798.45
$4p^4P_{\frac{1}{2}}$	59036.81			$4p'^2D_{\frac{3}{2}}$	47757.24
$4p^4D_{\frac{7}{2}}$	60225.45	$4p^2D_{\frac{5}{2}}$	57320.17	$4p'^2F_{\frac{7}{2}}$	48188.00
$4p^4D_{\frac{5}{2}}$	60591.48	$4p^2D_{\frac{3}{2}}$	57866.26	$4p'^2F_{\frac{5}{2}}$	48277.33
$4p^4D_{\frac{3}{2}}$	60848.28				
$4p^4D_{\frac{1}{2}}$	60999.51				

Terms based on SIII ^3P			Terms based on SIII ^1D		
			$s^2p^2 \cdot 3d$		
$3d^4F_{\frac{9}{2}}$	78058.19	$3d^2P_{\frac{3}{2}}$	70360.37		
$3d^4F_{\frac{7}{2}}$	78316.02				
$3d^4F_{\frac{5}{2}}$	78511.37	$3d'^2D_{\frac{5}{2}}$	69212.27		
$3d^4F_{\frac{3}{2}}$	78647.67	$3d'^2D_{\frac{3}{2}}$	69265.17		
		$3d^2F_{\frac{7}{2}}$	73221.76		
		$3d^2F_{\frac{5}{2}}$	73703.11		
			$s^2p^2 \cdot 4d$		
$4d^4P_{\frac{5}{2}}$	33005.80			$4d'^2G_{\frac{9}{2}}$	24171.53
$4d^4P_{\frac{3}{2}}$	32795.14			$4d'^2G_{\frac{7}{2}}$	24169.63
$4d^4P_{\frac{1}{2}}$	32676.09				
$4d^4D_{\frac{7}{2}}$	35410.80	$4d^2D_{\frac{5}{2}}$	29679.53		
$4d^4D_{\frac{5}{2}}$	35541.51	$4d^2D_{\frac{3}{2}}$	29841.18		
$4d^4D_{\frac{3}{2}}$	35622.66				
$4d^4D_{\frac{1}{2}}$	35670.67				
$4d^4F_{\frac{9}{2}}$	36208.98	$4d^2F_{\frac{7}{2}}$	31903.37		
$4d^4F_{\frac{7}{2}}$	36519.60	$4d^2F_{\frac{5}{2}}$	32385.52		
$4d^4F_{\frac{5}{2}}$	36729.90				
$4d^4F_{\frac{3}{2}}$	36864.80				
Terms combining with a^2D, a^2P, of s^2p^2 configuration					
$^1P_1$	~~48491.26~~ 48491.6	$^1P_1$	48661.7	^1x	55147.9

between the doublet and quartet systems have been detected the term values given in the two systems have not been determined accurately relative to each other.

Description of Table III

Table III gives a complete list of all the lines which have been classified in S II. In the first column is given the intensity of each line on a scale running from 0 to 10. Since the photographs were taken on different spectrographs the intensities are not in all cases comparable. The intensities of lines measured on the large grating spectrograph are prefixed by the letter R, the intensities of those taken from Kayser's tables are prefixed by K, and of those measured on the quartz spectrograph by Q. In general lines marked K are weaker than 0 lines on the R scale and those marked Q are weaker than either the K or R lines. Lines below 2000A are measured on the vacuum spectrograph. The second column of the table gives the wave-lengths, the third the wave-numbers, and the fourth and fifth the series designation in the quartet and doublet systems respectively.

Table III. *Classified lines of S II.*

Int.	I. A. Air	ν	Quartets	Doublets
R1	5819.22	17179.68		$4sP_2-4pD_2$
R3	5664.73	17648.21	$3dF_2-4pD_1$	
R4	5659.95	17663.11	$3dF_3-4pD_2$	
R6	5646.98	17703.68		$4sP_1-4pD_2$
K2	5645.70	17707.68	$4sP_2-4pD_2$	
R5	5640.32	17724.58	$3dF_4-4pD_3$	
R8	5639.96	17725.71		$4sP_2-4pD_3$
R1	5616.63	17799.34	$3dF_2-4pD_2$	
R6	5606.11	17832.74	$3dF_3-4pD_4$	
R1	5578.85	17919.88	$3dF_3-4pD_3$	
R4	5564.94	17964.67	$4sP_2-4pD_3$	
K1	5558.91	17984.14		$4pP_2-5sP_1$
R1	5556.01	17993.54	$4sP_2-4pD_1$	
K3	5536.76	18056.12	$3dF_2-4pD_3$	
R1	5526.22	18090.54	$3dF_4-4pD_4$	
K3	5518.76	18115.00		$4pP_1-5sP_1$
R5	5509.67	18144.88	$4sP_2-4pD_2$	
R5	5473.59	18264.49	$4sP_1-4pD_1$	
R10	5453.81	18330.72	$4sP_2-4pD_4$	
R9	5432.77	18401.71	$4sP_2-4pD_3$	
R5	5428.64	18415.72	$4sP_1-4pD_2$	
K3	5400.83	18510.54		$4pP_2-5sP_2$
R5	5345.67	18701.54		$4s'D_2-4p'F_3$
R7	5320.70	18789.31		$4s'D_3-4p'F_4$
R4	5212.61	19178.92		$4s'D_3-4p'D_3$
K2	5201.35	19220.45		$4s'D_3-4p'D_2$
R2	5201.00	19221.73		$4s'D_2-4p'D_2$
K1	5125.78	19503.82	$4pS_2-5sP_2$?	
R2	5103.30	19589.72	$4sP_2-4pP_2$	
R0	5047.28	19807.14		$4sP_2-4pP_1$
R5	5032.41	19865.67	$4sP_2-4pP_2$	
R3	5014.03	19938.49		$4sP_2-4pP_2$
R4	5009.54	19956.36	$4sP_2-4pP_1$	
R1	5006.71	19967.64	$4pS_2-5sP_2$	
R3	4991.94	20026.72	$4sP_2-4pP_2$	
R0	4942.47	20227.17	$4sP_1-4pP_1$	
R5	4925.32	20297.60	$4sP_1-4pP_2$	
R4	4924.08	20302.71	$4sP_2-4pP_2$	

TABLE III. (continued)

Int.	I. A. Air	ν	Quartets	Doublets
R2	4917.15	20331.33		$4sP_1-4pP_1$
R0	4901.30	20397.07	$4pP_2-5sP_2$	
R0	4900.47	20400.53	$4pP_2-5sP_1$	
R1	4885.62	20462.53		$4sP_1-4pP_2$
R0	4835.81	20673.30	$4pP_2-5sP_2$	
R3	4824.03	20723.79		$4pD_3-5sP_2$
R2	4819.55	20743.05	$4pP_1-5sP_2$ (Blend)	$4pD_2-5sP_1$
R9	4815.52	20760.41	$4sP_2-4pS_2$	
R3	4791.97	20862.43	$4pP_2-5sP_3$	
R2	4763.34	20987.82		$3dD_2-4p'F_3$
R3	4755.07	21024.32		$3dD_3-4p'F_4$
R0	4729.45	21138.21	$4pP_2-5sP_3$	
R7	4716.25	21197.37	$4sP_2-4pS_2$	
R0	4700.19	21269.80		$4pD_2-5sP_2$
R4	4668.59	21413.77		$3dD_3-4p'D_3$
R5	4656.75	21468.21	$4sP_1-4pS_2$	
R3	4648.14	21507.98		$3dD_2-4p'D_2$
R5	4552.37	21960.44		$4s'D_2-4p'P_1$
R6	4524.96	22093.46		$4s'D_2-4p'P_2$
R2	4524.65	22094.98		$4s'D_2-4p'P_2$
K1	4508.93	22172.03	$4pP_1-4dF_2$?	
K1	4492.32	22254.01	$4pS_2-4dD_3$	
R3	4486.63	22282.21	$4pD_2-5sP_1$	
R6	4483.42	22298.16	$4pD_3-5sP_2$	
R7	4463.58	22397.28	$4pD_4-5sP_3$	
R4	4456.39	22433.41	$4pD_1-5sP_1$	
R3	4432.37	22554.98	$4pD_2-5sP_2$	
R2	4431.00	22561.95		$3dP_2-4p'D_3$
K2	4402.64	22707.28	$4pD_1-5sP_2$	
R3	4391.81	22763.28	$4pD_3-5sP_3$	
R1	4333.84	23067.76	$4pP_2-4dD_2$	
R4	4318.64	23148.95	$4pP_2-4dD_3$	
R6	4294.39	23279.67	$4pP_2-4dD_4$	
R1	4291.43	23295.72	$4pP_2-4dD_1$	
R4	4282.60	23343.75	$4pP_2-4dD_2$	
R4	4278.51	23366.07	$4pP_1-4dD_1$	
R5	4269.72	23414.17	$4pP_1-4dD_2$	
R6	4267.76	23424.93	$4pP_2-4dD_3$	
R4	4230.94	23628.78		$4p'D_3-4d'G_4$
R4	4217.19	23705.82	$4pD_4-4dF_4$	
R4	4189.68	23861.59	$4pD_3-4dF_3$	
R5	4168.37	23983.46	$4pD_2-4dF_2$	
R10	4162.64	24016.47	$4pD_4-4dF_5$ (Blend)	$4p'F_4-4d'G_5$
R2	4162.29	24018.49		$4p'F_4-4d'G_4$
R10	4153.05	24071.92	$4pD_3-4dF_4$	
R5	4146.90	24107.62		$4p'F_3-4d'G_4$
R8	4145.05	24118.38	$4pD_2-4dF_3$	
R8	4142.24	24134.74	$4pD_1-4dF_2$	
R2	4050.08	24683.92	$4pD_4-4dD_3$	
R6	4032.77	24789.87	$4pS_2-4dP_3$	
R7	4028.74	24814.67	$4pD_4-4dD_4$	
R1	4009.35	24934.67		$4pD_3-4dF_3$
R1	4007.77	24944.50		$3dF_4-4p'F_3$
R2	4003.87	24968.80	$4pD_3-4dD_2$	
R5	3998.74	25000.84	$4pS_2-4dP_2$	
R6	3993.49	25033.70		$3dF_4-4p'F_4$
R5	3990.90	25049.95	$4pD_3-4dD_3$	
R4	3979.81	25119.75	$4pS_2-4dP_1$	
K3	3970.67	25177.58	$4pD_2-4dD_1$	
K2	3963.09	25225.72	$4pD_2-4dD_2$	
R0	3950.39	25306.82	$4pD_2-4dD_3$	
R2	3946.94	25328.94	$4pD_1-4dD_1$	
K1	3944.91	25342.00		$3dP_2-4p'P_1$
K1	3939.75	25375.20	$4pD_1-4dD_2$	

TABLE III. (continued)

Int.	I. A. Air	ν	Quartets	Doublets
R7	3933.25	25416.80		$4pD_3-4dF_4$
R3	3932.29	25423.30		$3dF_4-4p'D_3$
R5	3931.90	25425.82		$3dF_3-4p'F_3$
R1	3931.50	25428.41		$4pP_2-4dD_3$
R0	3924.07	25476.56		$3dP_2-4p'P_2$
R6	3923.43	25480.71		$4pD_2-4dF_3$
K1	3918.16	25514.99		$3dF_3-4p'F_4$
R1	3906.95	25588.19		bP_2-4pD_3
R5	3892.28	25684.63	$4pP_3-4dP_3$	
R4	3860.64	25895.13	$4pP_3-4dP_2$	
R0	3859.21	25904.72		$3dF_3-4p'D_3$
R2	3853.08	25945.93		$3dF_2-4p'D_2$
R3	3850.91	25960.55	$4pP_2-4dP_3$	
R1	3809.65	26241.70	$4pP_1-4dP_2$	
R1	3802.61	26290.29	$4pP_2-4dP_1$	
Q1	3734.8	26767.9		$4sP_2-4p'F_3$
R1	3672.11	27224.58		bP_1-4pP_1
R4	3669.03	27247.43		$4sP_2-4p'D_3$
K1	3663.36	27289.58		$4sP_2-4p'D_2$
K1	3654.52	27355.63		bP_1-4pP_2
R1	3638.17	27478.54		$4pD_3-4dD_2$
R4	3616.90	27640.13		$4pD_3-4dD_3$
Q5	3613.1	27669.4		bP_2-4pP_1
R3	3595.98	27800.93		bP_2-4pP_2
R3	3594.45	27812.76		$4sP_1-4p'D_2$
R3	3567.16	28025.53		$4pD_2-4dD_2$
Q3	3329.3	30027.6		$4sP_2-4p'P_1$
R1	3314.47	30162.09		$4sP_2-4p'P_2$
Q4	3272.3	30550.8		$4sP_1-4p'P_1$
Q3	3257.9	30685.5		$4sP_1-4p'P_2$
Q2	3015.7	33150.3		$4pD_3-4d'G_4$
Q1	2886.9	34628.9		$bP_2-4p'F_3$
Q3	2670.0	37442.4		$bP_1-4p'P_1$
Q1	2660.3	37578.8		$bP_1-4p'P_2$
Q1	2638.1	37894.5		$bP_2-4p'P_1$
Q2	2629.1	38024.7		$bP_2-4p'P_2$
	I. A. Vac			
5	1259.53	79394.8	aS_2-bP_3	
5	1253.79	79757.9	aS_2-bP_2	
3	1250.50	79968.0	aS_2-bP_1	
3	1234.14	81028.0		aP_2-bP_2
0	1233.36	81079.3		aP_1-bP_2
1	1227.45	81469.9		aP_2-bP_1
1	1226.70	81519.5		aP_1-bP_1
2	1131.65	88366.5		aP_2-4sP_1
2	1131.05	88413.1		aP_1-4sP_1
1	1125.00	88888.6		aP_2-4sP_2
1	1124.39	88937.3		aP_1-4sP_2
3	1102.32	90717.7		aD_3-bP_2
2	1096.57	91193.2		aD_2-bP_1
1	1031.34	96961.3		$aP_2-4s'D_{3,2}$
1	1030.87	97004.9		$aP_1-4s'D_2$
2	1019.53	98084.7		aD_2-4sP_1
2	1014.42	98578.0		aD_3-4sP_2
0	1014.09	98610.2		aD_2-4sP_2
2	1000.48	99952.3		aD_3-3dF_3
2	996.00	100401.9		aD_3-3dF_4
0	968.37	103265.9		aD_2-3dP_2
1	957.88	104397.5		$\begin{cases} aD_3-3dD_3 \\ aD_2-3dD_2 \end{cases}$
3	937.69	106644.8		$aD_3-4s'D_{3,2}$
3	937.41	106676.6		$aD_2-4s'D_{3,2}$
1	919.24	108785.8		aP_2-x

TABLE III. (continued)

Int.	I. A. Air	ν	Quartets	Doublets
3	918.82	108835.0		aP_1-x
3	912.74	109560.7	aS_2-4sP_1	
3	910.49	109830.3	aS_2-4sP_2	
3	906.87	110269.0	aS_2-4sP_3	
1	867.50	115273.7		aP_2-P_1
1	867.15	115320.5		aP_1-P_1
1	866.23	115443.3		aP_3-P_2
0	865.87	115491.1		aP_1-P_2
2	843.82	118508.5		aD_2-x
0	800.04	124993.9		aD_2-P_1
0	799.14	125134.6		aD_3-P_2
0	798.92	125168.8		aD_2-P_2
0	707.86	141271.0		aD_2-4dF_3
0	705.62	141720.1		aD_3-4dF_4
0	694.71	143944.9		aD_3-4dD_3
1	641.81	155810.0	aS_2-4dP_3	
0	640.93	156023.7	aS_2-4dP_2	
0	640.41	156149.9	aS_2-4dP_1	

No intercombinations between the doublet and quartet systems have been identified. The reason is doubtless that the data available in the present work did not include accurate measurements on the weaker lines among which such intercombinations are to be expected. Table IV gives a list of

TABLE IV. *Unclassified lines of S II.*

Int.	I. A. Air	ν	Int.	I. A. Air	ν
1	5142.33	19441.04	2	4185.90	23883.02
2	5027.19	19886.30	5	4174.25	23949.67
0	5011.61	19948.12	4	4173.97	23951.28
2	4779.09	20918.65	2	3860.11	25898.68
3	4561.87	21914.71	4	3831.37	26092.95
4	4549.56	21974.01	3	3783.13	26425.66
6	4464.44	22392.96	1	3678.11	27180.17
2	4431.00	22561.95	2	3385.79	29526.76
2	4259.15	23472.28	1	3371.87	29648.65
3	4257.39	23481.98	1	3368.07	29682.10
1	4193.50	23839.73	0	3356.40	29785.30

the only unclassified lines which can be definitely ascribed to S II. The group of lines in the region of 4200A probably involves the high $^2(S\,P\,D\,F\,G)$ terms of the $s^2p^2\cdot 4d$ configuration but it has not been possible to resolve them into multiplets. One line requires special mention, 4162.64, one of the strongest lines in the spectrum. It is without question the leading line of the multiplet $4p^4D$–$4d^4F$ and probably masks the line $4p'^2F_4$–$4d'^2G_5$ which should also be a strong line very close to this position. This line has been used to fix both the $4d^4F_5$ and $4d'^2G_5$ levels. The assumption of this value of the $^2G_5$ level gives an inverted G term of separation 1.90 cm^{-1}, a very reasonable value since in O II this term is inverted and has a separation of 1.2 cm^{-1}.

No terms from the configuration $s^2p^2\cdot 4f$ have been detected. Both the quartet and doublet terms based on the ^3P state of S III should be hydrogen-

like and hence have term values in the neighborhood of 27000. The doublet terms based on the ^1D term of S III should lie at about 15000. The combination of these terms with the terms of the $s^2p^2 \cdot 4d$ configuration will give faint lines in the red or infra-red whereas the combinations with the observed terms of the $s^2p^2 \cdot 3d$ configuration will give faint lines in the ultra-violet near 2000A where they might easily be missed.

Strong doublet lines in the extreme ultra-violet should arise from combinations between the low ^2D and ^2P terms and the doublet terms of the $s^2p^2 \cdot 4s$ and $s^2p^2 \cdot 3d$ configurations. These lines have been identified. The low terms should also combine strongly with the ^2P, ^2D and ^2S terms of the sp^4 configuration. An inverted ^2P term of separation 445 cm^{-1} at 82000 cm^{-1} which combines with the $s^2p^2 \cdot 4p$ doublet terms is doubtless the ^2P term of this group. Another ^2P term near 48000 and an unclassified term, x, at 55147.9 give strong lines in the extreme ultra-violet in combination with the low doublet terms.

One component P_2, of the $s^2p^2 \cdot 3d$ ^2P term could be definitely fixed by combinations with the $s^2p^2 \cdot 4p$ terms and with a^2P_2. The lines given by the P_1 member are doubtless too weak to be detected.

I am indebted to Dr. I. S. Bowen for the identification of two important multiplets in the extreme ultra-violet, a^4S_2–b^4P_{321} and a^4S_2–$4sP_{321}$ which were taken from unpublished data of his.

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EXTREME ULTRA-VIOLET SPECTRUM OF ARGON EXCITED BY CONTROLLED ELECTRON IMPACTS

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Abstract

Excitation of extreme ultra-violet spectrum of argon.—Circulating purified argon was excited by electrons from a Wehnelt cathode at various voltages up to 150 volts, with gas pressures of about 0.05 mm and currents of about 100 ma. Such excitation has been shown to arise from single rather than multiple electron impacts. The spectrum was photographed with the aid of a high vacuum spectrograph equipped with a glass grating. 88 lines, all believed due to argon, have been found in the wave-length region 1066 to 461. 20 of these belong to the known arc spectrum. Of the remaining 68 spark lines, 44 have not previously been reported. We fail to excite previously known A III lines, so that we attribute our 68 spark lines to A II.

Analysis of the argon spectrum.—37 spark lines have been classified. 12 of these classifications have been checked by numerous combinations involving lines in the near visible region (6883–2300). Tables of lines, terms and combinations are given. Three series of two members each give the series limit as 223, 363, so that the ionization potential is 27.82 ± 0.05 volts. Adding the first ioniozation potential 15.69 volts gives 43.51 volts as the minimum potential for double ionization. These refer to ionization to the $^3P_2$ limit, the lowest energy state of A III. A tentative term value of -33230 (relative to $^3P_2$) is given to the higher ^1D limit.

THE extreme ultra-violet spectrum of argon has been the subject of several investigations. First came the discovery of the resonance lines 1067 and 1048 by Lyman and Saunders,[1] and its verification by Hertz and Abbink.[2] Next came the discovery by Saunders[3] of 19 lines in the range 1067–849 and the identification of some of them as A I combinations between the low $3p^1S_0$ term and higher terms identified by Meissner[4] in his analysis of the near-visible spectrum. Dorgelo and Abbink[5] then carried out an exhaustive study of the extreme ultra-violet argon spectrum in arcs, glow discharges and condensed sparks at various pressures and voltages, and discovered some 40 new lines between 1067 and 519. They classified these lines as *arc* or *spark* according to their behavior under various conditions of excitation, and identified the term combinations responsible for 21 of the A I lines. They pointed out that the strong lines 932 and 920, and also two other pair of lines have nearly the wave number difference (about 1431) predicted by Meissner as the fundamental difference to be expected in the A II spectrum. One sextet, between 887 and 871, also found by Hopfield and Dieke,[6] has such a structure as to lead to its classification by

[1] Lyman and Saunders, Nature, **116**, 358 (1925).
[2] Hertz and Abbink, Die Naturwissenschaften, **14**, 648 (1926).
[3] Saunders, Proc. Nat. Acad. Sc., **12**, 556 (1926).
[4] Meissner, Zeits. f. Physik, **37**, 238 (1926); **39**, 172 (1926); **40**, 839 (1927).
[5] Dorgelo and Abbink, Zeits. f. Physik, **41**, 753 (1927).
[6] Hopfield and Dieke, Phys. Rev., **27**, 638 (1926).

by the latter authors as belonging to A III. Finally, Saunders[7] has investigated the way in which intensities of lines, relative to the resonance pair of A I, vary with excitation conditions, and has arrived at conclusions regarding arc or spark classification which are in some respects different from those of Dorgelo and Abbink, and has pointed out the peculiar intensity of the pair 932, 920 which are strong under apparent arc conditions although listed by Dorgelo and Abbink as spark lines.

Recent work with neon[8] showed us that spectral excitation by electrons from a hot cathode, in gas at low pressure, is peculiarly effective in exciting the first spark spectrum and in permitting use of highly purified gas. We therefore used this apparatus, which has been described elsewhere,[9] to investigate argon. The argon was purified by preliminary long arcing over a misch metal cathode, and this purification process was continued during all

TABLE I. $I(90)$ is intensity in pure argon at 90 volts; $I(110)$ is intensity in argon-helium mixture at 110 volts. Lines marked* are arc lines which have been classified by Saunders and by Dorgelo and Abbink. For significance of "?" see text. Terms followed by (^1S) or (^1D) go to these limits: all others go to ^3P limit. +line covered by He. $A_1 = 3p^5P_1$; $A_2 = 3p^5P_2$

λ	$I(90)$	$I(110)$	ν	Classification
1066.72	15	15	93745*	
1048.28	25	25	95394*	
1031.41	—	2	96954	
958.34	1d	–	104347	
931.97	7	7	107300	$A_1 - 5p^5\,{}^3S_1$
919.69	9	8	108732	$A_2 - 5p^5\,{}^3S_1$
894.27	4	–	111823*	
879.88	3	1	113652*	
878.68	–	1	113807	
876.00	4	1	114155*	
869.70	2	0	114982*	
866.77	4	2	115371*	
842.78	2	–	118655*	
834.45	6	2	119839*	
826.39	2	0	121008*	
825.42	1	0	121150*	
820.22	0	–	121918*	
816.32	4	2	122501*	
806.62	2d	1	123974*	
801.41	1	–	124780	
797.78	0	–	125348	
795.70	?	–	125675	
769 37	?	1	129976	—arc limit
762.37	2	–	131170	$A_1 - 3d^4D_3$
754.99	4	–	132452	$A_2 - 3d^4D_3$
755.21	–	0	132413	?
748.39	1	–	133620	$A_1 - 4s^4P_3'$
745.22	8	3d	134189	$A_2 - 4s^4P_3'$; $A_1 - 4s^4P_1'$
740.45	5	2	135053	$A_2 - 4s^4P_2'$
731.10	3	1	136780	$A_1 - 4s^2P_2'$
725.73	5	3	137792	$A_1 - 4s^2P_1'$
723.54	6	5	138209	$A_2 - 4s^2P_2'$
718.29	4	2	139219	$A_2 - 4s^2P_1'$
704.72	3	0	141900	$A_1 - 3d^4P_2'$?
699.00	4	1	143062	$A_2 - 3d^4P_3'$; $A_2 - 3d^4P_1'$
698.19	2	–	143227	$A_1 - 3d^2P_1'$?
697.82	1	–	143303	$A_2 - 3d^4P_2'$?
693.55	4	0	144186	$A_1 - 3d^2P_2'$?
691.29	1.5	–	144657	$A_2 - 3d^2P_2'$?
686.73	2	–	145618	$A_2 - 3d^2P_2'$?
679.59	6	4	147148	
678.17	4	0	147456	
676.48	5	1	147824	A_1 } $-3d\,(^4F', {}^2F',\ D)$
673.13	0	–	148560	A_2 }
672.03	6	4	148803	
671.21	6	3	148985	
666.23	5	2	150098	
664.84	2	0	150412	
662.11	6	3	151032	
637.52	–	1	156858	
612.59	4	2	163241	
603.11	2	2	165817	$A_1 - 3d(^1D)\,{}^2S_1$?
597.92	3	3	167246	$A_2 - 3d(^1D)\,{}^2S_1$?
584.53	1.5	+	171078	$A_2 - 3d(^1D)\,{}^2F_3'$?
583.65	3	+	171335	$A_1 - 3d(^1D)\,{}^2D_2$?
580.47	5	3	172264	$A_2 - 3d(^1D)\,{}^2D_3$?
578.81	1.5	1	172768	$A_2 - 3d(^1D)\,{}^2D_2$?
578.34	1.5	1	172909	$A_1 - 3d(^1D)\,{}^2P_2'$?
576.93	2	2	173331	$A_1 - 3d(^1D)\,{}^2P_1'$?
573.55	4	3	174353	$A_2 - 3d(^1D)\,{}^2P_2'$?
572.20	1	1	174764	$A_2 - 3d(^1D)\,{}^2P_1'$?
560.38	3	2	178450	
557.01	3	2	179530	
548.92	1	–	182176	$A_2 - 5s^4P_2'$
547.54	4	4	182635	$A_1 - 4s(^1D)\,{}^2D_2$?
546.36	2	1	183038	$A_2 - 5s^2P_2'$
543.96	1	1	183837	$A_2 - 4d^4D_3$
543.33	5	5	184050	$A_2 - 4s(^1D)\,{}^2D_2$?
538.47	–	0	185711	
537.18	1	+	186157	
530.65	1	1	188448	
526.54	0	–	189919	
524.83	3	3	190538	
522.93	2	3	191231	$A_1 - 3d(^1S)\,{}^2D_2$?
519.47	4	4	192504	$A_2 - 3d(^1S)\,{}^2D_2$?
514.43	1	0	194390	$A_1 - 4s(^1S)\,{}^2S_1$?
512.72	–	0	195038	
510.68	3	1	195817	$A_2 - 4s(^1S)\,{}^2S_1$?
503.78	0	–	198499	
502.20	0	–	199124	
491.09	0	–	203629	
490.76	2	3	203766	
489.26	0	1	204390	
488.88	2d	2	204549	
487.27	2	3	205225	
475.79	–	1d	210177	
464.20	–	1d	215424	$A_1 - 4d(^1D)\,{}^2P'_{1\frac{1}{2}}, 4d(^1D)\,{}^2D_2$?
461.11	–	1d	216868	$A_2 - 4d(^1D)\,{}^2P'_{1\frac{1}{2}}, 4d(^1D)\,{}^2D_{3\frac{1}{2}}$?

[7] Saunders, Proc. Nat. Acad. Sc., **13**, 596 (1927).

[8] Russell, Compton and Boyce, Proc. Nat. Acad. Sc., **14**, 280 (1928).

[9] Compton and Boyce, J. Frank. Inst., **205**, 497 (1928).

the exposures by forcing the circulating gas through the purifying bulb. Spectra of pure argon and of argon plus helium were photographed. The helium spark lines 303.81 and 256.33 (first, second and third orders) were used as primary standards and the arc lines 584.44, 537.12, 522.29, 515.70, 512.18, 510.07 508.72 (first and second orders) and 507.80, 507.13 (first order) as secondary standards of wave-length, thus giving calibration points all over the region of the spectrum investigated. Table I gives a list of the argon lines, their wave numbers, their intensities and their partial classification. At the shorter wave-lengths our measurements deviate slightly from those of Dorgelo and Abbink,[5] but we believe our values to be the better because of the wealth of helium standards used in this region.

The term arrangement of A II is similar to that of Ne II reported previously by us,[9] except for one important difference. In Ne II, only terms involving a displaced *s* electron exist in the group of next higher energy above the fundamental $2p^2P_{12}$ state. In A II on account of the additional completed outer shell of electrons, both 4*s* and 3*d* excited electron configurations exist at about the same levels above the fundamental $3p^2P_{12}$ state, so that the structure of the spectrum is very much more complicated than that of Ne II. Furthermore, a great part of the near-visible spectrum, most urgently needed for analysis, lies in regions which have not as yet been investigated or in which observations have not been made with sufficient precision.

With the wave-lengths of Table I, and the near-visible wave-lengths from Kayser's Handbuch, Vol. V and from L. Bloch, E. Bloch and G. Dejardin,[10] we have found about 150 combinations and thus identified a few of the A II terms. While this work was in progress, de Bruin[11] published a preliminary paper on the analysis of the near-visible spectrum, and we have used his results to correct our original mistake identification of some of the low s^4P terms. We have, in addition, found higher s^4P and d^4P terms, as well as s^2P terms, which permit three independent and consistent estimates of the ionization potential (to the p^3P_2 limit).

The following types of terms are predicted by the Hund theory. Fundamental terms $3p^2P_{21}$. Terms associated with $^3P_{210}$ limit: $s^4P'_{321}$, $p^4S'_2$, p^4P_{321}, $p^4D'_{4321}$, $d^4P'_{321}$, d^4D_{4321}, $d^4F'_{5432}$, $s^2P'_{21}$, $p^2S'_1$, p^2P_{21}, $p^2D'_{32}$, $d^2P'_{21}$, d^2D_{32}, $d^2F'_{43}$. Terms with ^1D limit: s^2D_{32}, p^2P_{21}, $p^2D'_{32}$, $p^2F'_{43}$, d^2S_1, $d^2P'_{21}$, d^2D_{32}, $d^2F'_{43}$, d^2G_{54}. Terms with ^1S limit: s^2S_1, p^2P_{21}, d^2D_{32}.

In Tables I and II the identifications *not* questioned are very likely correct, being checked by numerous intercombinations between higher terms. Those identifications marked "?" are suggested only as strongly indicated by the general spectral scheme of terms, intensities and frequency differences predicted by the Hund theory. In the absence of data permitting an adequate check by combinations which would be in the near infra-red or in the ultra-voilet beyond 2300, these identifications are only tentatively presented.

[10] L. Bloch, E. Bloch and G. Dejardin, Ann. de Physique **2**, 480 (1924).
[11] de Bruin, Zeits. f. Physik **48**, 62 (1928).

TABLE II. *Terms referred to $^3P_2$ limit as zero.*

Quartets					Doublets				
Term				Diff.	Term				Diff.
		to ^3P limit					to ^3P limit		
$3d$	D_4	91070.0	a		$3p$	P_2	223363	W	
				153.5					1430
	D_3	90916.5	b			P_1	221933	X	
				149.5	$4s$	P_2'	85153.6	A	
	D_2	90767.0	c						1014.6
				107.0		P_1'	84139.0	B	
	D_1	90660.0	d		$3d$	P_1'	78705	C?	
$4s$	P_3'	89156.0	e						−960
				844.9		P_2'	77745	D?	
	P_2'	88311.1	f						
				515.7	$3d$	D_3	73265	E?	
	P_1'	87795.4	g						314
$3d$	P_3'	80301	h?			D_2	72951	F?	
				241	$3d$	F_3'	72331	G?	
	P_2'	80060	i?						
	P_1'	—			$4p$	D_3'	64667.6	Y	
									663.7
$4p$	P_3	68354.4	s			D_2'	64003.9	Z	
				308.0					
	P_2	68046.4	t		$5s$	P_2'	40307.4	I	
				356.8					808.9
	P_1	67689.6	u			P_1'	39498.5	J	
$4p$	D_4'	65163.4	v		sp^2	$^2S_1$	114633		
				439.3					
	D_3'	65724.1	w				to ^1D limit		
				493.9	$3d$	S_1	56117	K?	
	D_2'	65230.2	x		$3d$	F_3'	52285	L?	
				260.3	$3d$	D_3	51099	M?	
	D_1'	64969.9	y						503
$4p$	S_2'	62348.8	z			D_2	50596	N?	
$5s$	P_3'	41803.5	j		$3d$	P_2'	49017	O?	
				627.8					417
	P_2'	41175.7	k			P_1'	48600	P?	
				729.1	$4s$	D_2	39313	Q?	
	P_1'	40446.6	l						15
$4d$	D_4	49722.6	m			D_2	39298	R?	
				122.3	$4d$	P_2'			
	D_3	49600.3	n				6502	S?	
				188.3		P_1'			
	D_2	49412.0	o						
				206.2					
	D_1	49205.8	p						
Other Limits							to ^1S limit		
$^3P_1-1110$ } from triplet PP' group of A III (Ref. 6, 7)					$3d$	D_3	30859	T?	
$^3P_0-1573$ }									158
						D_2	30701	U?	
^1D −33230					$4s$	S_1	27545	V?	
^1S −?									

Table II gives the spectral terms and Table III indicates the combinations which have been identified. We have also found a number of additional combinations which we are as yet unable to identify.

TABLE III. *A II Combinations (o found by de Bruin).*

	W X	Y Z	s t u		z	W X	Y Z	s t u	v w x y	z	
a		x	o	o o		x x	x x		x	x	*A*
b	x	x x	o o	o o o		x x	x		x		*B*
c	x	x x	o o o	o o o							
d			o o	o o		x x					*C*
						x x					*D*
e	x	x x	o o	o o o	o						
f	x x	x x	o o o	o o o	o	x					*E*
g		x	o o	o o	o	x x					*F*
h	x					x					*G*
i	x x										
						x	x x	x	x	x	*I*
j		x	x x	x x	x		x	x	x x	x	*J*
k	x	x	x x x	x x	x						
l			x x	x x	x	x x					*K*
m			x	x x		x					*L*
n	x	x	x x	x x							
o		x x	x x x	x x		x					*M*
p			x x	x x		x x					*N*
						x x					*O*
						x x					*P*
						x					*Q*
						x					*R*
						x x					*S*
						x					*T*
						x					*U*
						x x					*V*

The following brief outline is given of the reasons for the questionable identifications. Lines 698, 693, 691, 686 form a characteristic doublet PP' group with the fundamental 1431 frequency difference, but with intensities which suggest inversion of the upper pair of terms. The position of these lines is such that they come from the set of terms belonging to the ^3P limit. The only unfilled place for a PP' group in the Hund scheme is a $d^2P'_{12}$ combination with the fundamental p^2P_{12} terms. Furthermore, the corresponding pair of terms in Ne II has actually been found to be inverted. Thus we feel reasonably sure of this identification. The three lines 704, 699, 697 form a group of slightly lower frequency than the above group. Since we always find quartet terms a little lower than doublet terms of the same type, we naturally classify these lines as arising from d^4P' terms, which is supported by the fact that intensities and separations are consistent with this view.

Just to the high frequency side of these lines is a group of seven strong and two faint lines. There can be no doubt that these include the lines from the remaining $3d$ terms (^2D, $^4F'$, $^2F'$), but there is little evidence on which to base a classification, so that they are not given individual identification in the Tables. The only accurate 1431 frequency difference is between lines 671 and 664. These, together with 666 might arise from $3d^2D$, or with 662 might arise from inverted $3d^2D$ terms. $3d^2F$ would give only one line, and $3d^4F$ would give three lines. Possibly 679 and 673 belong to this latter system, but their frequency difference seems to depart more from 1431 than we should expect. Further spectroscopic work in the near-infra-red is needed to complete the classification of this group of lines.

After a considerable gap there next comes a group of fairly strong lines between 612 and 572. These are of too low frequency to be second members of any series going to the ^3P limit and too high to be first members of such series: furthermore all possible first members have already been accounted for. Thus they must be the first members of series associated with the higher limits ^1D or ^1S. These lines are therefore ascribed to series with ^1D limit, since these would be expected to be lower in frequency than series belonging to ^1S, and since the structure of the group can be explained only in this way. Lines 603, 597 have the right separation and intensities to indicate their origin in $3d^2S_1$. Lines 578, 576, 573, 572 for a doublet PP' group, which can only arise from the term $3d^2P'$. Lines 583, 578 have the 1431 separation and, with the intervening stronger line 580, form a perfect multiplet if ascribed to the $3d^2D$ terms. The isolated remaining line 584 can be only one thing, $3p^2P_2-3d^2F_3'$. These identifications take care unambigously of all $3d$ electron terms. The lines from the expected $4s^2D$ terms are almost certainly the strong pair 547, 543, which come among the second members of the ^3P limit series, but are very much stronger. We should expect three lines, the one of shorter wave-length being weakest and the next, close to it, being strongest. We find only two, and their separation is only 1415. This suggests that the weakest line was too weak to detect, and that the terms $4s^2D_2$ and $4s^2D_3$ are only about 15 frequency units apart. The two shortest lines found, 464, 461, come just right to be the second members of the series $3p^2P_{12}-m\ d^2P'_{12}$, if the quantum defect for a d electron is the same for this series as for the d electron series going to the ^3P limit. This identification is therefore likely, and enables the ^1D limit to be calculated as -33230.

Finally the remaining strong group 524 to 510 must by exclusion, and by position and structure, be the first members of the two series going to the ^1S limit. The pair 514, 510 have close to the 1431 frequency difference and are believed to arise from the $4s^2S_1$ term. The pair 522, 519 are probably the two strong members of the triplet group due to $3d^2D$.

There remain, unexplained, a fairly strong isolated line 612, a pair 560, 557 of separation 1080, a distinctive group 490, 489, 488, 487 which looks like a PP' group but is yet not quite right, and several other faint lines. None of these has been reported for any other element, and we have

not found them in working with helium or neon. Neither do we find *any* known line of any other element on our plates. Consequently we believe them to be argon lines. They may belong to A III, but we do not find any trace of the A III sextet already found by Hopfield, Dieke and Saunders. In fact we have made several attempts, by using high voltage and long exposure, to excite these A III lines by single electron impact, but without success. Similarly our source apparently gives no N III or Ne III, so that we have come tentatively to the conclusion that single electron impacts do not excite the second spark spectrum, even though the voltage is ample. We are thus without a clue as to the origin of these remaining lines.

The ionization potential corresponding to the $s^2p^4\ {}^3P_2$ limit, and giving the low state of A III, is 27.82 ± 0.05 volts (223,363 frequency units). This limit falls between the approximate "Rydberg" limits calculated from the s and d electron series respectively, since the Ritz correction term is opposite in sign in the two cases. Since the first ionization potential is 15.69 volts, the minimum potential for double ionization is 43.51 volts, in good agreement with the experimental value of 45.3 ± 1.5 volts found by Barton[12] and somewhat higher than values predicted from indirect evidence.[13]

The peculiar intensity of the pair 931,919 noted by Saunders[7] is due to its peculiar mode of excitation, which is by ionization involving the removal of an s electron. It is also interesting to notice that Mohler[13] did not find photoelectric ionization of argon at a voltage corresponding to the excitation of this pair, although he found strong ionization by the corresponding pair in neon.[9] The explanation of this is that this pair in argon is of longer wave-length than the arc limit, whereas in neon it is of shorter wave-length.

We are glad to acknowledge the valuable suggestions and assistance of our colleague, Professor Shenstone.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.
June 2, 1928.

[12] Barton, Phys. Rev., **25**, 469 (1925).
[13] Mohler, Phys. Rev., **28**, 46 (1926).

THE ASSIGNMENT OF QUANTUM NUMBERS FOR ELECTRONS IN MOLECULES. I

By Robert S. Mulliken

Abstract

Quantum numbers, notation, closed shells, molecular states.—The problem of making a complete assignment of quantum numbers for the electrons in a (non-rotating) diatomic molecule is considered. A tentative assignment of such quantum numbers is made in this paper (cf. Table III) for most of the known electronic states of diatomic molecules composed of atoms of the first short period of the periodic system. The assignments are based mainly on band spectrum, and to a lesser extent on ionization potential and positive ray, data. The methods used involve the application and extension of Hund's theoretical work on the electronic states of molecules. Although the actual state of the electrons in a molecule, as contrasted with an atom, cannot ordinarily be expected to be described accurately by quantum numbers corresponding to simple mechanical quantities, such quantum numbers can nevertheless be assigned formally, with the understanding that their mechanical interpretation in the real molecule (obtainable by an adiabatic correlation) may differ markedly from that corresponding to a literal interpretation. With this understanding, a suitable *choice of quantum numbers* for a diatomic molecule appears to be one corresponding to an atom in a strong electric field, namely, quantum numbers n_τ, l_τ, σ_{l_τ}, and $s_\tau (s_\tau = 1/2$ always) for the τ'th electron, and quantum numbers s, σ_l, and σ_s for the molecule as a whole (σ_{l_τ} and σ_s represent quantized components of l_τ and s, respectively, with reference to the line joining the nuclei). These quantum numbers may be thought of as those associated with the imagined "united atom" formed by bringing the nuclei of the molecule together. A *notation* is then proposed whereby the state of each electron and of the molecule as a whole can be designated, e.g. $(1s^s)^2\ (2s^p)^2\ (2s^s)^2\ (2p^p)$, ^2P for a seven-electron molecule with $\sigma_l = 1$, $s = 1/2$; in a symbol such as $2s^p$ the superscript denotes l_τ, the main letter, σ_{l_τ}, thus $2s^p$ means that the electron in question has $n_\tau = 2$, $l_\tau = 1, \sigma_{l_\tau} = 0$. Electrons with $\sigma_{l_\tau} = 0, 1, 2, \cdots$, are referred to as $s, p, d, \cdots$, electrons. It is shown that in a molecule it is usually natural to define a group of equivalent electrons giving a resultant $\sigma_l = 0$, $s = 0$ as a *closed shell*; in this sense, two s electrons, or four p, or d, $f, \cdots$, electrons form a closed shell. The possible *molecular states* corresponding to various electron configurations are deduced by means of the Pauli principle (cf. Table I, and Appendix).

Promoted electrons, binding energy, bonding power, and relation of molecular to atomic electron states.—As Hund has shown, some of the electrons must undergo an increase in their n values (principal quantum numbers) when atoms unite to form a molecule. Such electrons are here called *promoted electrons*. The electrons in a molecule may be classified according to their *bonding power*, positive, zero, or negative. Electrons whose presence tends to hold a molecule together, as judged by the fact that their removal from a stable molecule causes a decrease in the energy of dissociation D or an increase in the equilibrium internuclear separation r_0 may be said to have *positive bonding power*, and are identified with, or defined as, *bonding electrons*. The definitions of bonding power in terms of changes of D, and of changes of r_0, are unfortunately not in general equivalent, and we must accordingly distinguish "energy-bonding-power" and "distance-binding-power". On the whole, promoted electrons should tend to show negative energy-bonding-power, unpromoted electrons positive energy-bonding-power, but much should depend on "orbit dimensions."

Certain rules governing the relations of the electronic states of a molecule to those of its dissociation products are discussed; in addition to theoretical rules established by Hund in regard to σ_l and s values, another, presumably less strict, rule is here proposed, namely that the σ_{l_r} values of all the atomic electrons before union should be preserved in the molecule (σ_{l_r} *conservation rule*). Selection rules for electronic transitions are also discussed; in addition to rules given by Hund, the following are proposed: $\Delta l_r = \pm 1$ for intense transitions; $\Delta\sigma_{l_r} = 0, \pm 1$.

Results.—The key to the assignment of quantum numbers made here is found in the fact that the molecules BO, CO^+, and CN show an *inverted* ^2P state instead of the normal ^2P which should occur if this state were analogous to the ordinary ^2P states of the Na atom. The existence of such a low-lying inverted ^2P indicates that in these molecules there exists a closed shell of p electrons from which one is easily excited. It is concluded that this is a $(2p^p)^4$ shell. The identification of two other closed shells, of s electrons, very likely $(3s^p)^2$ and $(3s^s)^2$, follows; the electrons in these and the $(2p^p)^4$ shell are roughly equal in energy of binding. According to this interpretation, the electron jumps involved in the band spectra of BO, CN, CO^+, and N_2^+ are more analogous to X-ray than to optical electron transitions. From this beginning, proceeding to CO, N_2, NO, O_2, O_2^+, F_2, C_2, etc., a self-consistent assignment of quantum numbers is built up for most of the known states of the various molecules treated in this paper. The spectroscopic analogies of CN, N_2, NO, etc., to Na, Mg, Al are justified and the partial failures of these analogies, such as the chemical resemblance of CN to a halogen, are explained. Nearly all the hitherto observed ionization potentials of the molecules discussed can be accounted for by the removal of a *single* electron from one or another of the various closed shells supposed to be present. The N_2^+ band fluorescence produced by short wave length ultraviolet light (Oldenberg) is accounted for as the expected result of photo-ionization of a $3s^p$ electron. The steadily decreasing heat of dissociation in the series N_2-NO-O_2-F_2 is accounted for by the successive addition of promoted $3p^p$ electrons with strong negative bonding power. Starting from N_2, whose normal state corresponds to a ^1S configuration of closed shells, we add one $3p^p$ electron to give the ^2P normal state of NO and O_2^+, two to give the ^3S normal state of O_2, four to give a closed shell, $(3p^p)^4$, which accounts for the ^1S normal state of F_2.

In N_2 (probably also in O_2 and the other homopolar molecules, but data are too few), band systems for which $\Delta l_r \neq 1$ are notably lacking, thus giving support to Hund's predicted selection rule for homopolar molecules; in the analogous heteropolar molecule CO, many systems occur with $\Delta l_r = 0$, although they are probably weaker, as expected, than those for which $\Delta l_r = \pm 1$. On account of this strict selection rule in N_2, certain levels should be metastable, in particular the final level of the afterglow (α) bands of *active nitrogen*. There is evidence for the existence of a strict selection rule $\Delta s = 1$ in homopolar molecules.

Introduction

LANGMUIR,[1] in 1918, in elaborating G. N. Lewis' theory of valence,[2] suggested that the peculiar stability and inertness of the N_2 molecule might be accounted for by the following assumptions: (*a*) each N nucleus retains its two most firmly bound electrons, i.e., each atom keeps its innermost or K shell; (*b*) eight of the remaining ten electrons form a group of eight or "octet," i.e. an L shell, or complete group of two-quantum electrons, in the language of Bohr's theory; (*c*) the last two electrons form a

[1] I. Langmuir, J. Am. Chem. Soc., **41**, 868, 1543 (1919); **42**, 274 (1920).

[2] G. N. Lewis, Valence and the Structure of Atoms and Molecules. 1923. Chemical Catalogue Company.

pair which is imprisoned in this octet and helps to stabilize the whole structure. To CO and CN^-, with the same number of electrons, Langmuir attributed similar, although of course less symmetrical, structures. The surprising stability of NO, with one more electron, Langmuir explained by a similar structure, but with three electrons imprisoned in the octet.

If the octet in these pictures really functions as an L shell, the additional electrons might be regarded as "imprisoned" valence electrons. From this point of view, the molecules CN, CO or N_2, and NO should have respectively one, two, and three valence electrons. In this, they would be exactly like the atoms Na, Mg, Al. No marked analogy is evident in chemical behavior, however. Chemically, CN resembles Cl rather than Na, as shown especially by the stability of CN^-; and N_2 resembles argon[1] rather than Mg. This is attributable to the fact that the supposed valence electrons are "imprisoned," i.e. much more firmly held than the valence electrons of Na, Mg, Al.

Nevertheless, as the writer has pointed out,[3] the band spectra of CN and a number of other "one-valence-electron" molecules (CO^+, N_2^+, BO, etc.) indicate a marked analogy between these molecules and the Na atom, in respect to the nature and arrangement of electron levels. Similarly, as Birge has shown,[4,5] the electron levels of CO and N_2 present a remarkable analogy to those of Mg. Further, as first shown by Sponer's work, the NO energy levels parallel those of the Al atom.[4,5,6]

If the suggested analogies are correct, they should be capable of expression by specifying a definite "orbit" for each electron in the molecule. For example, each electron in CN or BO should have quantum numbers the same as those of a corresponding electron in the Na atom, except that the molecules mentioned have two extra K electrons. In discussing such an assignment of quantum numbers,[7,5] the writer pointed out[7] that in the formation of such a molecule from two atoms, some of the electrons must undergo rather radical changes in their quantum numbers.

Birge and Sponer,[8] however, have obtained strong evidence that a molecule such as CO or N_2, if merely given sufficient energy of vibration, can dissociate smoothly into its atoms. This at first seemed to conflict with the conclusion stated at the end of the preceding paragraph, since in the old quantum theory there seemed to be no way in which quantum numbers could be changed except by violent agencies such as collision or light absorption. Birge and Sponer's results seemed, then, to demand a model composed of atoms with unchanged quantum numbers.[5]

[3] R. S. Mulliken, Phys. Rev. **26**, 561 (1925).

[4] R. T. Birge, Nature, Feb. 27, 1926.

[5] R. S. Mulliken, Phys. Rev. **28**, 493–7 (1926).

[6] Cf. F. A. Jenkins, H. A. Barton and R. S. Mulliken, Phys. Rev. **30**, 150 (1927) for discussion and bibliography.

[7] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 338 (1926).

[8] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926). H. Sponer, Ergebnisse der exakten Naturwissenschaften, **6**, 75 (1927). R. T. Birge, International Critical Tables.

But Hund has now shown that, with the new quantum theory, these contradictions disappear. In fact Hund's work,[9,10,11,12] together with that of Heitler and London,[13,14] promises at last a suitable theoretical foundation for an understanding of the problems of valence and of the structure and stability of molecules. For example, Hund's work enables us to understand how a continuous transition can exist between ionic and atomic binding. Briefly, the molecule may be said to be latent in the separated atoms; in a certain sense, the molecular quantum numbers already exist before the atoms come together, but take on practical importance, at the expense of the atomic quantum numbers, only on the approach of the atoms to molecular distances.[10] This of course does not exclude the possibility that in some cases a quantum jump in the usual sense may be needed to reach the *most stable* state of the molecule.

Purposes

The present work represents an attempt to obtain a detailed knowledge of quantum numbers and energies of individual electrons in molecules, similar to that which we now possess in the case of atoms. The present paper is confined to the discussion of diatomic molecules composed of atoms of the first short period. Of the molecules and molecular states here discussed only a few are the stable states of chemically stable molecules. But aside from their purely theoretical interest, the numerous excited states and chemically unstable molecules discussed are indispensable in deducing the electron configurations for those special cases which correspond to stable molecules; and are also important as intermediate steps in chemical reactions.

Stability, molecular and chemical. In this connection it seems desirable to bring out a distinction not ordinarily made. Chemical stability of a molecule implies not merely that two or more atoms have united to a single stable molecule, but further, that such a molecule is stable in an assemblage of its fellows, or in a mixture with other molecules. For example, a single NO molecule is exceedingly stable with respect to N+O, but NO gas is unstable with respect to a gas composed of N_2 and O_2 molecules. The most stable state of a *single molecule* composed of specified atoms in given numbers is merely that of minimum *energy;* probably all molecules, even He_2 from normal He atoms, are capable of some stability in this sense (*molecular stability*). The most stable state of a *system of molecules* is one of ultimate statistical equilibrium, i.e., one of minimum *free energy;* this corresponds to *chemical stability.*

[9] F. Hund, Zeits. f. Physik, **36,** 657 (1926).

[10] F. Hund, Zeits f. Physik, **37,** 742 (1927).

[11] F. Hund, Zeits. f. Physik, **42,** 93 (1927).

[12] F. Hund, Zeits. f. Physik, **43,** 805 (1927).

[13] W. Heitler and F. London, Zeits f. Physik, **44,** 455 (1927). Cf. also Y. Suguira, Zeits. f. Physik, **45,**484 (1927) and S. C. Wang, Phys. Rev. **31,** 579 (1928) for further detailed calculations on H_2.

[14] W. Heitler, Zeits. f. Physik, **46,** 47 (1927), **47,** 835 (1928); F. London, Zeits. f. Physik, **46,** 455 (1927).

Methods

Throughout the present paper, even when no specific reference is made, the essential ideas and methods are those so successfully used by Hund.[9,10,11] As compared with Hund's papers, the chief difference is in the attempt to assign individual electronic quantum numbers. This has required some additional assumptions, and it is possible that the results obtained may be far from correct. Nevertheless the writer believes that they have at least a certain degree of correspondence to the truth and that this will prove of value for the ultimate accomplishment of the objective aimed at.

Interpolation between two limiting cases, namely (*a*) two separate atoms, (*b*) the "united-atom" formed by the hypothetical process of bringing the nuclei of the separate atoms completely together, has proved valuable in arriving at conclusions about the electronic states of a diatomic molecule. For the application of the Pauli principle to determine the maximum possible number of electrons for any given set of quantum numbers the correlation with the united-atom is all-important. The possible quantum number assignments for the molecule should be obtainable from those of the united-atom by imagining the latter to be placed in a strong, non-uniform but axially symmetrical electric field, corresponding to the effect of separating the united-atom nucleus into the two nuclei which exist in the molecule. But the *energy-order* of terms corresponding to various quantum numbers may be expected to differ, often very greatly, from that appropriate to an atom in a strong electric field. For example, we shall ordinarily expect the electron distribution of the normal state of the molecule to correspond to that of some *excited* state of the united-atom, and vice versa.

Deviations from the energy-order of the united-atom are especially to be expected in the case of electrons for which an increase in the principal quantum number n has been forced by the formation of the molecule, but for which no correspondingly large energy changes have occurred, so that the energies lie close to those characteristic of the separated atoms. This condition should exist especially in loosely-bound molecules; and always for inner electrons which are not essentially shared by the two nuclei.

Bohr's method of determining electron configurations in atoms by imagining all electrons removed, and then returning them one by one, each to the available orbit of lowest energy, is less easily applicable to molecules on account of the difficulties in predicting binding energies for various orbit-types. But, once a body of information in regard to binding energies has been built up on the basis of spectroscopic and other facts, this method should be helpful.

Before attempting to determine the electron configurations of individual molecules, we must first consider what possibilities are to be expected theoretically. The discussion falls naturally under two heads: (1) matters in which the molecule resembles the united-atom, (2) those where the correlation is mainly with the separate atoms. Under the first head come such questions as those of notation and the nature of the quantum numbers

appropriate to molecules, nature of closed shells, and of molecular states and multiplets. Under the second head come energy relations, and the question as to what particular electronic states of a molecule may be expected from the union of two atoms each in a specified state. These two groups of questions will be taken up successively in the two following sections of the paper, after which the results will be applied to specific examples.

Quantum Numbers, Notation, Closed Shells, and Molecular States

Quantum numbers. In the case of an atom, it is customary first to assign quantum numbers n, l, and s for each electron, then to fix the state of the atom as a whole by specifying how the individual l's and s's are coupled.[15] Usually most of the electrons are in "closed shells." In the present paper it will be assumed somewhat arbitrarily that each electron in a molecule, in particular the τth electron, can be characterized by four quantum numbers, n_τ, l_τ, σ_{l_τ}, and s_τ ($s_\tau = \frac{1}{2}$ always), where σ_{l_τ} corresponds to the space-quantized component of l_τ in the direction of the figure axis. In addition, the resultants σ_l, s, and $\sigma(\sigma = \sigma_l + \sigma_s$, where σ_s is the component of s along the figure axis), must be specified,[16] these quantum numbers being applicable to the molecule as a whole, somewhat like l, s, and j in the case of the atom. This choice of quantum numbers corresponds to one of those proposed by Hund.[9] It is strictly appropriate only for the imagined case of a non-rotating molecule, but, after adding rotational and vibrational quantum numbers j and n, the proper quantum numbers for any actual case (cf. Hund's papers[9,10,11]) can be obtained by means of an adiabatic correlation.

[It should be pointed out that the quantum number σ_l as used here is identical in meaning with σ_k as used by the writer in other papers on "Band Structure and Electronic States." The notation is here changed for the sake of consistency with the use of the quantum numbers l_τ.]

Throughout the present paper, however, the molecule is to be thought of as though the nuclei were fixed, since we are not directly interested here in the effects of nuclear rotation and vibration.[16,17] In the study of electronic states and quantum numbers we shall, nevertheless, make very frequent use of information which has been gained by a study of band structure.

Just as, in atoms, the ordinary l_τ, l, s, j assignment corresponds only to an ideal limiting case, so in molecules, even with fixed nuclei, the assignment proposed is strictly appropriate only for an ideal special case. Although for atoms, the ideal case is usually (not always) closely approached,[15] the same cannot be said for molecules: rather it appears that, in molecules, no one limiting case is ordinarily approached, but that the actual condition usually

[15] Cf. F. Hund, Linienspektren und Periodisches System der Elemente. 1927 Julius Springer

[16] When the molecular rotation is considered, the coupling of s and σ_l may be broken down (Hund's case b)[9], leading to a different arrangement of the terms, in which σ_s and σ are lost.

[17] Born and Oppenheimer have shown (Ann. der Physik, **84**, 457, 1927) that this separation, in imagination, of nuclear from electronic motions, leads to no serious errors.

lies more or less in the midst of a region between several limiting cases. An adiabatic correlation can, however, always be imagined between the quantum numbers here used and others which, for a particular electron in a particular molecule, may be physically more appropriate.

In general, the quantum numbers l_τ and σ_{l_τ} must not be regarded as corresponding at all accurately to angular momenta and angular momentum components respectively. Nevertheless, the use of such quantum numbers, especially the σ_{l_τ}'s, seems to fit fairly well the behavior of the molecules studied in the present paper, and it seems likely that they represent a good compromise which is reasonably appropriate for the "average molecule."

Meaning of quantum states of electrons in new mechanics; quantum phases. In accordance with the new quantum mechanics, the assignment of independent quantum numbers for the various electrons is of course to be taken in the same qualified or figurative sense as is required for atoms. That is, each quantum state of an individual electron in such an assignment is supposed to be merely a *phase* through which *each* of the electrons of the molecule goes repeatedly. We might better speak of the quantum phases than of the quantum states of electrons.

Notation. A notation designating the "quantum numbers for each electron" will be helpful. Designations such as $1s^s$, $2s^s$, $2s^p$, $2p^p$, $3s^s$, $3s^p$, $3s^d$, $3p^p$, $3p^d$, $3d^d$, will serve this purpose. Here the number denotes n, while the main letter refers to σ_{l_τ} and the superscript letter to l_τ. If a superscript is identical with its main letter, it may be omitted if there is no danger of confusion with the atomic notation. The complete designation of the electron state of a molecule would then be given as in the following examples:

$$(1s^s)^2\,(2s^s)^2\,(2s^p)^2\,(2p^p)^4\,(3p^p),\ {}^2P;$$
$$(1s^s)^2\,(2s^s)^2\,(2s^p)^2\,(2p^p)^3\,(3s^s)^2,\ {}^2P;$$
$$(1s^s)^2\,(2s^s)^2\,(2s^p)^2\,(2p^p)^4\,(3s^s)\,(3p^d),\ {}^3P^D \text{ or } {}^1P^D$$

As in the case of atoms, abbreviations will no doubt subsequently be adopted to denote various frequently occurring configurations. The designations ${}^2P$, ${}^3P$, etc., are those already adopted previously[18] for describing the resultant state of a molecule, and are analogous to those used for atoms except that the letter (S, P, etc.) denotes the resultant value of σ_l instead of that of l. A superscript letter, as D in ${}^3P^D$, can be added to indicate the resultant l for the corresponding united-atom, if this l is known. The reason for relegating l_τ and l to superscripts and placing the emphasis on σ_{l_τ} and σ_l is that the analysis of band spectra yields directly[19] only the value of σ_l (and of s).

Closed shells and molecular states. In an atom one ordinarily speaks of two equivalent s electrons, six equivalent p electrons, ten equivalent d electrons, as forming a closed shell, the latter being defined as a completed group of equivalent electrons having $l=0$ and $s=0$. In a strong electric field, or in a molecule, the l couplings are broken down and each electron tends to ac-

[18] Cf. R. S. Mulliken, Phys. Rev. **29**, 648–9 (1927).

[19] According to methods described in a series of papers (Phys. Rev. 1926–7) and in accordance with Hund's theoretical work.

quire a quantum number σ_{l_τ}. Considering a shell of six equivalent p electrons by way of example, two electrons now have $\sigma_{l_\tau}=0$, two have $\sigma_{l_\tau}=+1$, two have $\sigma_{l_\tau}=-1$. The two electrons with $\sigma_{l_\tau}=0$ should now have a markedly different energy than the other four, being probably more firmly bound, and are naturally set apart as forming an independent closed shell, with $\sigma_l=0$, $s=0$. The remaining four electrons should be alike in energy, since $\pm\sigma_{l_\tau}$ makes no difference in energy in an electric field; they may be regarded as forming a single closed shell, again with $\sigma_l=0$ and $s=0$. Similarly, an atomic closed shell of ten equivalent d electrons should split in the molecule into three closed shells each with $\sigma_l=0$ and $s=0$; one of these should consist of two electrons each with $\sigma_{l_\tau}=0$, another of four electrons with $\sigma_{l_\tau}=\pm1$, the third of four electrons with $\sigma_{l_\tau}=\pm2$.

As is well known from the work of Pauli, Hund, and others, the resultant state of an *atom* is determined exclusively by the *electrons which are not in closed shells*.[15] If *only* closed shells are present, the atom is in a ^1S state ($l=0$, $s=0$). Analogous statements are true for molecules, if we here define a closed shell as the smallest complete group of electrons having $\sigma_l=0$ and $s=0$. A molecule with a given assignment of electron states for the individual electrons may in general be as a whole in any one of several different states, depending on relative orientations among the σ_{l_τ}'s and s_τ's belonging to shells which are not closed. *E.g.*, if there is a system of closed shells plus two $3p^p$ electrons, the possible molecular states are ^1D, ^3S, and ^1S. Table I gives a summary of the possible molecular states corresponding to various electron configurations, including those likely to be met with in the molecules considered in the present paper. The occurrence of normal and inverted multiplets should probably usually be in agreement with Table I, but in this feature occasional exceptions may be expected, especially when more than one kind of electron with $\sigma_{l_\tau}>0$ is present. The method by which the results of Table I are obtained is given in an Appendix at the end of this paper.

TABLE I. *Possible molecular states for various electron configurations.*

Configuration	States	Configuration	States	Configuration	States
(As)	^2S	$(As)\,(Bp)^3$	^3P_i, ^1P	$(Ap)\,(Bd)$	^3F_n, ^3P_n, ^1F, ^1P
$(As)\,(Bs)$	^3S, ^1S	$(Ap)\,(Bp)$	^3D_n, ^3S, ^1D, ^1S	$(Ap)^2\,(Bd)$	^4D_n, ^3D_i, ^3G_n, ^3S, ^3D_n
(Ap)	^3P_n	$(Ap)^2\,(Bp)$	^4P_n, ^3P_n, ^3F_n, ^3P_i, ^2S	$(Ap)^3\,(Bd)$	^4F, ^3P_n, ^1F, ^1P
$(Ap)^2$	^3S, ^1D, ^1S	$(Ap)^2\,(Bp)$	^3D_i *or* $_z$, ^3S, ^1D, ^1S	(Ad)	^3D_n
$(Ap)^3$	^3P_i	$(Ap)^2\,(Bp)^2$	^4S, ^3S, ^1S, ^1D_z, ^3S, ^1G, ^1D, ^1S	$(Ad)^2$	^3S, ^1G, ^1S
$(As)\,(Bp)$	^3P_n, ^1P	$(Ap)^3\,(Bp)^2$	^4P_i, ^2F_n, ^2P_n, ^2P_i, ^2P_i	$(Ad)^3$	^2D_i
$(As)\,(Bp)^2$	^4S, ^2S, ^2D_z, ^2S	$(Ap)^3\,(Bp)^3$	^3D_i, ^3S, ^1D, ^1S	$(As)\,(Bd)$	^2D_n, ^1D

Notes. (*a*) Each configuration given is understood to include, in addition to the electrons specified, any number of *closed shells* such as $(Xs)^2$, $(Xp)^6$, or $(Xd)^{10}$. (*b*) A symbol such as As stands for *any* s electron state, as $3s^2$, $4s^3$, $3s^{4f}$, etc.; similarly with Bp, etc. (*c*) The subscripts n and i stand for normal and inverted, and z for a very small, multiplet separation. (*d*) States corresponding to some additional configurations can be obtained by noting that the addition of a non-equivalent s electron merely alters the *multiplicity*, by ±1.

Shells of two. The *ultimate* shell, as London has emphasized (ref. 14, p. 468) is the "*shell of two*," i.e., two electrons alike in n_τ, l_τ, and σ_{l_τ} (including the *sign* of σ_{l_τ}), but having their spins antiparallel. Such a two-shell is not necessarily a closed shell according to the ordinary meaning of the latter term. Thus for $n=2$, there are four shells-of-two: (*a*) $(2s^s)^2$, with $l=0$,

$\sigma_l=0$, $s=0$; (*b*) $(2s^p)^2$, with $\sigma_l=0$, $s=0$; (*c*) $(2p^p)^2$ with $\sigma_l=-2$, $s=0$; (*d*) $(2p^p)^2$ with $\sigma_l=+2$, $s=0$. Here (*a*) and (*b*) are closed shells in the ordinary sense for a molecule, while (*c*) and (*d*) must be taken *together* to give a molecular closed shell, with $\sigma_l=0$; (*b*) must be added to (*c*) and (*d*) to give an atomic closed *p* shell, with $l=0$.

Energy Relations. Relation of Molecule to Separated Atoms

Promotion of electrons. When a molecule such as CN is formed from its atoms, some of the electrons of the separated atoms must evidently suffer an increase in their n values, in order to satisfy the demands of the Pauli principle for the molecule and united-atom (the united-atom corresponding to CN is Al). An electron whose n has been increased in this way will be called a "*promoted*" electron.

Hund has shown, in terms of the new mechanics, how such a promotion comes about.[10] For the two center problem (*e.g.*, H_2^+), which is separable in elliptical coördinates (ξ, η, ϕ), the increase in n results from an increase in the quantum number n_η. In this relatively simple case, n_η is correlated with n_θ of spherical coördinates for the united atom, since if the two centers are forced together, the ellipses $\xi=$const. go over into spheres ($r=$const.) and the hyperbolas $\eta=$const. into cones ($\theta=$const.). Hence, since $l=n_\theta+n_\phi$, increase in n by promotion, in the formation of H_2^+, should be accompanied by increase in l. But in more complex molecules it seems likely from Hund's work that the correlation $n_\eta \rightarrow n_r$ may also occur; if so, l would *not* increase with n during promotion (Cf. Appendix, p. 220, for further details). At present the theory leaves us in uncertainty as to which, if either, correlation is usually preferred.

Energy relations; binding energies. The energy E of a (non-rotating, non-vibrating) molecule may conveniently be thought of as divided into (*a*) positive potential energy of repulsion of the nuclei and (*b*) negative energies ("binding energies"), of each electron in the field produced by the nuclei and other electrons. A necessary condition for the formation of a molecule is evidently that, as the distance r between the nuclei is reduced, the total binding energy (*B.E.*) of the electrons must at first *increase faster* than the nuclear energy (*N.E.*). At $r=r_0$, the two rates of increase become equal and the total energy has a minimum, while for $r<r_0$ the nuclear repulsion energy increases faster than the electronic binding energies. The energy of dissociation (D^v of Table III) is evidently given by the relation

$$D^v(=E_{r_0}-E_\infty)=[(B.E.)_{r_0}-(B.E.)_\infty]-[(N.E.)_{r_0}] \qquad (1)$$

For the formation of a reasonably stable molecule, i.e., one for which D^v is fairly large, *B.E.* must evidently increase *considerably* faster than *N.E.* over a *considerable range* of r values, as r decreases toward r_0. As a corollary, r_0 must usually be fairly small in stable molecules. The converse proposition that molecules with small r_0 necessarily have large D^v is, however, not true—

as can, for example, be seen by a comparison of the data for states X and B of CO (Table III).

Each molecular state has a different $E(r)$ curve and a different D^v. Although the $E(r)$ curves show a great variety of forms, any such curve may be characterized to a considerable extent by giving the values of r_0, ω_0 (the vibration frequency), and D^v:

$$(d^2E/dr^2)_{r_0} = (2\pi c\omega_0)^2\mu, \text{ and } D^v = \int_{r_0}^{\infty} E(r)dr.^{21}$$

For a given molecule, it is not even necessary to state r_0 and ω_0 separately, since $\omega_0 r_0^2$ has been found empirically to be approximately constant for each molecule.[22] (There is as yet no theoretical explanation for this somewhat surprising relation.)

Any $E(r)$ curve may be thought of as jointly determined by all the electrons in the molecule. Strictly speaking, we cannot divide the electronic energy into a sum of energies of individual electrons, since much of the energy is really mutual energy of different electrons. Nevertheless it is convenient to think of the, often large, changes in $E(r)$ produced by displacing a single electron from one orbit to another as being caused by changes in a $B.E.(r)$ curve of the displaced electron, corresponding to the assumed relation

$$E(r) = N.E.(r) + B.E.(r) = N.E.(r) + \sum_r [-B.E.(r)]_r \qquad (2)$$

The effect of any particular type of electron orbit on $E(r)$ may be judged by the effects, on D^v and r_0 or ω_0, of removing this electron or displacing it to another orbit. According to the results of the present investigation, as given in Table III, each occupied orbit-type has a rather specific effect on these quantities.

As the distance between the nuclei is steadily decreased, during the union of two atoms, the binding energy of any unpromoted electron may usually be expected to increase steadily, since the electron comes under the influence of a steadily increasing effective charge; the latter would reach a maximum if the nuclei were united. For a promoted electron, however, the increase in effective charge is at least partially, and often more than, offset by the direct and indirect effects of the increase in n, so that the binding energy may be either increased or decreased on union of the nuclei. This will be made clear by the following examples. (1) Suppose two normal H atoms can unite to form a 2^3S^P excited hydrogen molecule, one electron being promoted to $n=2$ (cf. "Discussion of Heitler and London's work," below). For the separate atoms, the binding energy of each electron is 13.53 volts, or a total of 27.06 volts for both. The united-atom (helium) would probably be in a 2^3P state,[10] or possibly in a 2^3S state. For present purposes it makes no difference which of these possibilities is correct. Assuming a 2^3P state, the energy of removal of the promoted electron is 3.6 volts,[20] while for the

[20] Cf. A. Fowler, Report on series and line spectra. London, 1922. Also ref. 15.

[21] Cf. e.g. E. Condon, Phys. Rev. **28,** 1182 (1926).

[22] R. T. Birge, Phys. Rev. **25,** 240 (1925); R. Mecke, Zeits. f. Physik, **32,** 823 (1925).

subsequent removal of the other electron the energy is 54.1 volts (ionization potential of He^+). Thus while the promoted electron is more loosely bound than before union of the nuclei, the total binding energy, 57.7 volts, is over twice as great as for the separate atoms. By interpolation, similar statements are probably true for the molecule at all stages of approach of the nuclei. If it were not for the mutual repulsion of the nuclei, the two atoms should apparently unite completely to a single atom.[24] (2) If two many-electron atoms unite to form a molecule, one may expect to find that the binding energy is increased, usually at least, for all the unpromoted electrons, but that it may be either increased or decreased for the promoted electrons. Whether an increase or a decrease in binding energy occurs on promotion might be expected to depend largely on the relative shapes and sizes of the orbits in question, also on the values of n (e.g., promotion from $n=1$ to $n=2$ is energetically much more important than from 2 to 3). Roughly speaking, if $n>1$ initially, a decreased binding energy might be expected if promotion is to a non-penetrating orbit, but an increased energy if to a highly penetrating orbit.

Bonding electrons and bonding power. In chemistry, the electrons of a molecule are often thought of as divided into two classes, (*a*) "bonding" electrons, in pairs,[2] which hold the molecule together, and (*b*) "non-bonding" electrons, which do not. While the present work (cf., however, London[14]) does not indicate any such sharp division in general, it is nevertheless possible to assign, in a rough approximate way, various degrees of "*bonding power*" for various orbit-types. For this purpose, electrons whose presence in a molecule tends to make D^v large, or r_0 small, as judged by the fact that their *removal* from a stable molecule causes decrease in D^v or increase in r_0, may be said to have positive bonding power, or to be bonding electrons; and conversely. (In practise large ω_0 may be used as an alternative criterion for positive bonding power in place of small r_0, since as noted above, ω_0 varies inversely as r_0^2.) The two criteria of positive bonding power just suggested (large D^v, and small r_0 or large ω_0) are often, but unfortunately not in general, equivalent; we have for example $r_0=1.15$ *A*, $D^v=11.2$ volts for state X of CO, and $r_0=1.12$ *A*, $D^v=2.8$ volts (or perhaps only 0.5 volts) for state B of CO (cf. Table III). The very different $E(r)$ curves, in spite of equal r_0, in states X and B of CO, may perhaps be attributed to differences in orbit dimensions and hence in the form of the *B.E.*(r) curve, for the electron whose orbit differs in the two cases.

To distinguish between the above two definitions of bonding power we may speak of the *energy-bonding-power* of an electron, as judged by its effect on D^v, and of its *distance-bonding-power*, as judged by its effect on r_0. Although the energy definition of bonding power is perhaps the more appropriate, it suffers from two difficulties: (*a*) in case the two molecular states to be compared give *different* dissociation products (e.g., excited atoms in the one case but not in the other), the definition is not altogether satisfactory; (*b*) the values of D^v are for the most part not known at all accurately as yet.

For these reasons the more convenient definition of bonding power is that in terms of r_0 or ω_0, ω_0 being used in practise since it is the easier to determine.

The energy-bonding-power of an electron is intimately related to the change in its binding energy during molecule formation (cf. Eqs. (1) and (2), and accompanying discussion). From this fact and the preceding discussion of *B.E.*'s of promoted and unpromoted electrons, it is evident that unpromoted electrons should on the whole show positive energy-bonding-power, and promoted electrons the reverse; and that D^e should on the whole be largest for molecules having the smallest relative number of promoted electrons. This can be applied in the following way: if D^e is markedly decreased by transfer of an electron to a certain orbit, this may be taken as evidence that the latter orbit represents a promoted condition of the electron.

Corresponding statements can, unfortunately, not be made with the same definiteness in respect to the distance-bonding-power.

Relation of orbit dimensions to energy-bonding-power and energy changes in molecule-formation. If r is the distance between the nuclei, and d is, roughly speaking, the diameter of the "electron orbit," the binding energy of an electron must obviously be a function of r/d rather than of r. Only when r_0 is small, yet large enough so that r_0/d is comparable with unity for a given electron, should we expect a large change in energy and "orbit shape" (better, in the Schrödinger ψ function) for this electron on formation of a molecule.

Except where very light atoms (H, He, Li) are present, $d/r_0 << 1$ for the K shells of the two atoms in a diatomic molecule. For example, in CN, $r_0 = 1.172\ A$ for the normal state, while the Bohr diameters of the K orbits of the C and N atoms respectively are about $0.24\ A$ and $0.20\ A$. In the CN molecule, two of the electrons remain as $1s^e$ electrons, while two must technically be promoted, probably becoming $2s^p$ or $2s^e$ electrons. Although for the united-atom ($r = 0$) corresponding to CN the energy and other changes would be large for these electrons, they are relatively, and probably absolutely, small at the value $r = r_0 = 1.17$. Hence, as Hund puts it, it "has sense" to speak of these electrons still as K electrons (cf. ref. 10, p. 763).

For the L orbits of carbon and nitrogen, with diameters[23] of the order of $1.1 - 1.5\ A$, $d/r_0 \sim 1$, and relatively if not absolutely much larger energy and other changes should occur when the atoms unite than in the case of the K orbits. If, on the other hand, we consider the formation of a CN molecule from a C atom containing a *large* orbit such as a $3d$ orbit ($d \sim 9\ A$), we now have $d/r_0 >> 1$, so that, again, there should be (for this orbit) very little change in energy or other characteristics during molecule formation.

The factors of "orbit shape" and "degree of penetration" should also be important. E.g., an "elliptical" $2s^e$ orbit might be expected to show a greater increase in binding energy than a "circular" $2p^p$ orbit with its "plane" perpendicular to the internuclear axis, because the elliptical shape permits a closer approach to both nuclei, assuming equal areas for the two orbits and $r_0 \sim d$. Hence an unpromoted $2s^e$ electron might be expected to show greater

[23] For the areas swept out, in the case of the "elliptical orbits."

energy-bonding-power than an unpromoted $2p^p$ electron. A similar difference might be expected between a $3s^s$ and a $3p^p$ electron; if, as is the case in the molecules discussed in present paper, $3s^s$ and $3p^p$ are promoted electrons, the energy-bonding-power might of course be small or negative for both, but would be expected to be much less negative for $3s^s$ than for $3p^p$. These ideas are borne out by the results given in Table III.

Promotion energies. A specific example will be helpful in introducing the convenient concept of "promotion energy." In a nitrogen molecule, there are, among others, probably two $2s^s$ electrons and two $3s^p$ electrons. In each of the two N atoms from which this N_2 molecule was formed, there were two $2s$ electrons, or a total of four $2s$ electrons, all being equally firmly bound. Suppose two of these remain unpromoted and become $2s^s$ electrons of N_2, while the other two are promoted to give the $3s^p$ electrons of N_2. We expect to find the binding energy of the $2s^s$ electrons greater than before union of the two atoms; the binding energy of the $3s^p$ electrons may, perhaps, be either greater or less than in the atoms. In any case we expect to find that the promoted, $3s^p$, electrons are less firmly bound than the unpromoted, $2s^s$, electrons. The higher energy of the $3s^p$ as compared with the $2s^s$ electrons, we shall define as the "*energy of promotion*" of these electrons. This promotion energy should ordinarily increase steadily as r decreases; of principal interest, however, of course, is the promotion energy for $r=r_0$. Although we cannot in general define the promotion energy of a promoted electron in quantitative terms as in the example given, the concept can always be used in at least a qualitative way.

Discussion of Heitler and London's work. Heitler and London have shown[13] that two normal hydrogen atoms interact in two ways: (*a*) they show attraction and form a normal hydrogen molecule (1^1S), or (*b*) they show strong repulsion in a ^3S configuration. The difference between these two cases comes about as an effect analogous to Heisenberg's quantum-mechanical "resonance." Heitler and London label the ^3S condition 1^3S and consider that it is not a true state of the molecule, and that it corresponds to an impossible state of the united-atom (helium).[24] So far as the writer can see, however, the correct designation of this state is 2^3S, in accordance with conclusions of Hund.[10,24] The repulsion of the two atoms at moderate distances is then connected with the large promotion energy required to reach 2^3S, and r_0 is merely large, but not non-existent.

Heitler and London have further concluded that a state of repulsion is a fundamental characteristic (but cf. London[25]) of any two atoms or molecules at least one of which is composed solely of electronic "shells of two" (cf. above). They cite He+He, He+H, H_2+H, etc., the normal state being meant in each case. Yet it seems obvious, from the existence of Van der Waals attractive forces in helium, that very unstable molecules must be

[24] In their first paper, Heitler and London seem, *tacitly*, to imply that what is here called "promotion" of electrons does not exist. But in his most recent paper (Zeits. f. Physik **47**, p. p. 839, footnote), which appeared after the present paper had gone to press, Heitler accepts the (Hund) point of view stated above.

possible even in such cases.[25] In other similar cases, there is evidence that more or less stable molecules exist. Thus the low ^2S state of HgH, with a heat of dissociation of 0.4 volts, is without much doubt formed from a normal Hg and a normal H atom. Again, the ^2D state of CH, which possesses high stability ($r_0 = 1.11 \times 10^{-8}$ cm) is probably formed from a normal H atom and a ^1D carbon atom, although the latter is composed exclusively of shells of two. These considerations, however, give no reason for disputing Heitler and London's conclusions,[13,14]—which are moreover in harmony with those of Hund,—that two molecules such as He+He or He+H should show only one mode of interaction, and that two atoms such as Li+H, H+H, Li+Li, should show just two, contrasting, modes of interaction.

Correlation of molecular quantum numbers with those of separate atoms. Hund has suggested[11] the following procedure for determining the possible states of a molecule which can be obtained by bringing together two atoms initially in specified states. Assume each atom to be placed in a strong electric field so that quantum numbers σ_l and σ_s are established ($\sigma_l = l, l-1, \cdots 0, \cdots -(l-1), -l$; $\sigma_s = s, s-1, \cdots -s$). Then all the possible values of σ_l and σ_s for the molecule are respectively given as algebraic sums of the σ_l and σ_s values of the two atoms. The possible s values for the molecule comprise all values lying between s_1+s_2 and s_1-s_2, inclusive, where s_1 and s_2 refer to the separate atoms;[26] i.e., the s values correspond to the possible *vector* sums of s_1 and s_2.

Consider for example a $(1s)^2(2s)^2(2p)$, ^2P boron atom and a $(1s)^2(2s)^2(2p)^4$, ^3P oxygen atom. The ^2P boron state ($l=1$, $s=\frac{1}{2}$) should give rise in a strong electric field to six components ($\sigma_l = 0, \pm 1$ with $\sigma_s = \pm\frac{1}{2}$), and the ^3P oxygen atom ($l=1$, $s=1$) to nine ($\sigma_l = 0, \pm 1$, with $\sigma_s = 0, \pm 1$). Some of these components fall together in pairs or threes, but this can be avoided by imagining a temporary magnetic field placed parallel to the electric axis. (Without this the σ_s values given, for $\sigma_l = 0$, lack meaning; also $\pm\sigma_l$ states fall together; cf. Appendix for details). For the BO molecule formed from B(^2P) plus O(^3P), the number of strong field states formed by all possible combinations of the atoms in their various states is 6×9, or 54. This conclusion is based on Hund's principle[10,11] that in the formation of a molecule from two atoms "no state is lost." The 54 strong-field components, during withdrawal of the imagined magnetic field, group themselves into a number of molecular electronic states, as follows: three ^2S states ($\sigma_l = 0$, $s = \frac{1}{2}$, $\sigma_s = \pm\frac{1}{2}$) and three ^4S states ($\sigma_l = 0$, $s = 1\frac{1}{2}$, $\sigma_s = \pm\frac{1}{2}, \pm 1\frac{1}{2}$); two ^2P ($\sigma_l = \pm 1$, $s = \frac{1}{2}$) and two ^4P ($\sigma_l = \pm 1$, $s = 1\frac{1}{2}$); one ^2D and one ^4D ($\sigma_l = \pm 2$). These results have been given by Hund.[11]

We can go further than Hund in predicting the electron configuration of the molecule if we specify the individual σ_{l_r} value for "each electron" (or strictly, in the new quantum mechanics, of each quantum phase,—cf. above,

[25] Possibly in some cases not, if vibration and rotation are taken into account. At the end of his second paper,[14] London refers briefly to the question of Van der Waals forces.

[26] To permit resultants other than s_1+s_2 and s_1-s_2, one must here allow the possibility of a breaking up of the original spin couplings.

p. 192) in each atom, and assume that these are all preserved in the molecule. It seems likely that this assumption (the "*detailed* σ_{l_τ} *conservation rule*") should usually if not always hold.

In order to apply this assumption, we first note that the state of each of the two *atoms*, in the imagined strong electric field before they are brought together, can be described according to the strong-field quantum numbers and notation adopted above for *molecules*. Thus the six strong-field components from B(^2P) may be grouped under $(1s^s)^2(2s^s)^2(2s^p)$, $^2S^P$, with two components, corresponding to $\sigma_l=0$, $\sigma_s=\pm\frac{1}{2}$ in a magnetic field; and $(1s^s)^2(2s^s)^2(2p^p)$, $^2P^P$, with four magnetic components, corresponding to $\sigma_l=\pm1$, $\sigma_s=\pm\frac{1}{2}$. Similarly the nine components from O(^3P) fall under $(1s^s)^2(2s^s)^2(2s^p)^2(2p^p)^2$, $^3S^P$, corresponding to $\sigma_l=0$, $\sigma_s=0$, ±1, and $(1s^s)^2(2s^s)^2(2s^p)(2p^p)^3$, $^3P^P$, corresponding to $\sigma_l=\pm1$, $\sigma_s=0$, ±1.

In applying the σ_{l_τ} conservation rule, it is useless to specify the n_τ and l_τ values of the electrons, since we do not in general expect these to be preserved when the molecule is formed. It is therefore sufficient to give, for each atomic strong-field state, the *total* number of s, p, or d electrons, where s, p, or d indicates $|\sigma_{l_\tau}|=0$, 1, or 2. Thus we may classify $(1s^s)^2(2s^s)^2(2s^p)$ of boron, i.e., B($^2S^P$), as an s^5 configuration, and $(1s^s)^2(2s^s)^2(2s^p)^2(2p^p)^2$ of oxygen, i.e., O($^3S^P$), as an s^6p^2. The addition of these should give a BO molecule of the $s^{11}p^2$ *configuration class*, in a ^2S or ^4S state. Similarly, B($^2S^P$) plus O($^3P^P$) should give ^2P and ^4P of the $s^{10}p^3$ class, since O($^3P^P$) is s^5p^3. Likewise, B($^2P^P$) plus O($^3S^P$) should give an additional ^2P and ^4P of the $s^{10}p^3$ class, while B($^2P^P$) plus O($^3P^P$) should give two ^2S, two ^4S, one ^2D, and one ^4D state of the s^9p^4 class.

A qualification in regard to the σ_{l_τ} conservation rule should be noted, as follows: if (for example) an s^4p and an s^6p^2 atom are found to give an $s^{10}p^3$ molecule, we know directly from this fact only that the *total numbers* of s and p electrons have been conserved, but not that σ_{l_τ} has been conserved for each *individual* "electron" or "quantum phase." Nevertheless it seems reasonable in most cases to infer detailed conservation of σ_{l_τ}'s as the cause of observed conservation of total numbers of s, p, $\cdots$ electrons. Such an inference will, however, in general, *not be implied* in the following discussion when reference is made to the "σ_{l_τ} conservation rule." The inference may be explicitly avoided by referring to the "*non-detailed* σ_{l_τ} *conservation rule.*"

In Table II the σ_l and s values and the σ_{l_τ} configurations obtained in a strong electric field are given, implicitly or explicitly, for the lowest energy states of the atoms of the first short period. From this information the possible σ_k and s values, and, in so far as our assumption is correct, the possibilities in respect to configuration class, can be predicted for any molecule formed from two such atoms (cf. Note 2 of Table II).

Knowing the n and l values for the atoms,[15] each configuration-class formula in Table II is sufficient to determine the *detailed* configuration for the atomic state in question, including the value and sign of each σ_{l_τ}. Consider for example s^5p^2, ^2S from N(^2D). Since N(^2D), in the *atomic* notation, is $(1s)^2(2s)^2(2p)^3$, the complete configuration here must, in the molecular

notation, be $(1s^s)^2(2s^s)^2(2s^p)(2p^p)^2$, and since $\sigma_l=0$, the two $2p^p$ electrons must have $\sigma_{l_r}=+1$ and -1 respectively. Similarly s^5p^3, ^3P from O(^3P) must be

TABLE II. *Atomic configurations for a strong electric field.*

Li, ^2S: s^3, ^2S	Li, ^2P: s^3, ^2S and s^2p, ^2P	
Be, ^1S: s^4, ^1S	Be, ^3P: s^4, ^3S and s^3p, ^3P	Be, ^1P: s^4, ^1S and s^3p, ^1P
B or C^+, ^2P: s^5, ^2S and s^4p, ^2P		
C or N^+, ^3P: s^3p, ^3P and s^4p^2, ^3S		
^1D: s^4 (or s^4p^2?), ^1S and s^3p, ^1P and s^4p^2, ^1D		
^1S: s^4p^2 (or s^6?), ^1S		
N or O^+, ^4S: s^3p^3, ^4S		
^2D: s^3p^3, ^2S and s^4p^3 (or s^6p?), ^2P and s^3p, ^{22}D		
^2P: s^3p^3, ^2S and s^6p (or s^4p^2?), ^2P		
O, ^3P: s^3p^2, ^3S; s^3p^3, ^3P		
^1D: s^3p^3, ^1S; s^3p^3, ^1P: s^6p^2, ^1D		
^1S: s^4p^4, ^1S		
F, ^2P: s^3p^4, ^2S and s^6p^3, ^2P		

Notes. (1) The results given in this table are obtained by methods similar to those used in the application of the Pauli principle for atomic multiplets in making the correlation between strong and vanishingly weak magnetic fields.[15] These methods are modified in a way appropriate to electric fields (cf. Table V, in the Appendix). (2) For the resulting *molecule* the following cases are important (in each case the statement made holds for *each value of s* which is possible): (*a*) if $\sigma_l=0$ for one atom, and $|\sigma_l|=q$ for the other, one molecular state with $|\sigma_l|=q$ results; (*b*) if $|\sigma_l|>0$ for both atoms, two molecular states result, each of double weight because corresponding to $\pm\sigma_l$, one with $|\sigma_l|=|(\sigma_l)_2|+|(\sigma_l)_1|$, the other with $|\sigma_l|=|(\sigma_l)_2|-|(\sigma_l)_1|$, where $(\sigma_l)_1$ and $(\sigma_l)_2$ refer to the two atoms, and $|(\sigma_l)_2|\geqq|(\sigma_l)_1|$; except that, (*c*) if $|(\sigma_l)_2|-|(\sigma_l)_1|=0$, a state of double weight is replaced by *two* states of unit weight with $\sigma_l=0$; an example of (*c*) is the case of $B(^2P^P)$ plus $O(^3P^P)$, discussed above.

$(1s^s)^2(2s^s)^2(2s^p)(2p^p)^3$; and since $\sigma_l=\pm1$, two of the $2p^p$ electrons must have $\sigma_{l_r}=\pm1$, while the third must have $\sigma_{l_r}=\mp1$.

WORKING RULES

With the background sketched above, we are now ready to formulate a set of working rules to be used in the analysis of spectroscopic and other data for the purpose of assigning quantum numbers to electron states of actual molecules.

Ionization energies of individual electrons. Other things being equal, the energy required to remove an electron of any specified type (e.g., $3s^p$) may reasonably be expected to change regularly as the atomic number of one or both atoms is gradually altered, unless the promotion status of the electron should change. Unpromoted electrons should always, or usually, be more firmly bound in the molecule than in the atom, while promoted electrons may be either more or less firmly bound.

Multiplet separations. For the total width $\Delta\nu$ of a molecular multiplet, values are to be expected which approximate those for equally firmly bound electrons in the constituent atoms. As Mecke has shown, the molecular $\Delta\nu$, in its dependence on the atomic number Z, usually represents a compromise between the two atoms.[27] In a general way, $\Delta\nu$ may be expected to depend on Z and on an effective quantum number n^* according to the Landé formula (cf. ref. 15, p. 61). More specifically—provided the electrons concerned are fairly well shared—$\Delta\nu$ should be proportional to $(Z_a^{*2}+Z_b^{*2})/n^{*3}$, where Z^*

[27] R. Mecke, Naturwiss. **13**, 755 (1925); Zeits. f. Physik, **36**, 795 (1926); **42**, 416–22 (1927). E. Hulthén, Nature **116**, 642 (1925).

represents the effective nuclear charge (corrected for shielding) of atom a or b. Thus in particular $\Delta\nu$ should decrease rapidly with increasing n^*.

Bonding power of electrons. Unpromoted electrons whose "orbits" are of the order of size of r_0 should show strong energy-bonding power. Electrons in large non-penetrating orbits should be as good as ionized, and should show zero energy-bonding power. Promoted electrons should show small or negative energy-bonding power unless orbit size or other conditions are very favorable.

Relation of molecule to separate atoms. The atoms into which a molecule in a given state can dissociate must be in states which have l and s values compatible with the σ_l and s values of the molecule (cf. Table II and accompanying discussion). Also, these atoms should, usually at least, be in states capable of yielding σ_{l_r} configurations (cf. Table II) of such classes that their sum agrees with the σ_{l_r} configuration class of the molecule. For a pair of atoms in specified electronic states a definite number of molecular states of each (σ_l, s) type can be predicted (cf. Table II), and this number cannot be exceeded; a similar but less strict rule should hold in regard to configuration classes.

Electron impact. Processes in which only one electron is removed or excited should be more probable than those involving two electrons.

Selection rules for radiation transitions. (1) Leaving out of account the selection rules for j, j_k, σ_s, etc., which determine the internal structure of bands, the only fairly strict[28] rule to be expected for ordinary molecules is $\Delta\sigma_l = 0$ or ± 1. (2) As in atoms, $\Delta s = 0$ should be greatly preferred unless the (l, s) or (σ_l, s) coupling is large (large multiplet separations). (3) For the same reasons as in atoms, jumps in which only one electron changes its quantum numbers (n_r, l_r, and σ_{l_r}) should be much more common than those involving changes for two or more electrons. (4) To the extent that the l_r's are good quantum numbers, $\Delta l_r = \pm 1$ should hold as for atoms; in case there is also strong coupling of l_r's, a second electron might sometimes make a simultaneous jump such that $\Delta l_r = 0$ or ± 2. (5) In so far as the l_r's are not too strongly coupled, so as to suppress the individual σ_{l_r}'s, the latter should individually obey a selection principle $\Delta\sigma_{l_r} = 0$ or ± 1. The same result follows automatically from (1) and (3). (6) (Additional selection rules for symmetrical molecules.) For symmetrical molecules a strict rule should hold according to which at least one of the three transitions conceivable between three electron levels is always absent.[11] This is equivalent to (*a*) assigning a symmetry quantum number n_s for *each electron state* and probably, at least when rule (3) above is followed, for *each electron*, and then (*b*) specifying the selection rule $\Delta n_s = \pm 1, \pm 3, \cdots$. For the case of H_2^+, n_s can probably be identified with l, as Hund has shown[11]; we shall tentatively assume[29]

[28] But in case molecular states exist where the effect of the electric axis is very small, σ_l ceases to exist, and with it the selection rule for σ_l, —cf. Hund's case *d*.[9]

[29] In the case of separability in elliptical coordinates, as in H_2^+, n_s is to be identified with $(n_\eta + n_\phi)$, which goes over into $(n_\theta + n_\phi) = l$ on union of the nuclei. But this particular correlation of quantum numbers in elliptical and spherical coordinates cannot be relied upon in general

that n_{s_τ} can be identified in general with l_τ. If, or when, this is true, the rule $\Delta n_{s_\tau} = \pm 1, \pm 3, \cdots$, practically coincides with a *strict* applicability of $\Delta l_\tau = \pm 1$, at least to the extent of completely cutting out $\Delta l_\tau = 0$ and ± 2.[30]

Assignments of Electron Configurations for Known Molecules

Introductory. As outlined in the introduction, the writer suggested that the electronic states of certain "one-valence electron molecules" (BO, CO^+, CN, N_2^+) are analogous to those of the sodium atom. Subsequently Hund showed that the suggested analogy is entirely consistent with the possibility that each of the molecules named can dissociate directly, by increase in the vibrational quantum number, into normal or slightly excited atoms.

For each of the four molecules named, three electronic states are known; an unexcited and an excited ^2S state, and between these a ^2P state,[3,5]—except that the ^2P has not yet been observed in N_2^+. The excitation potentials of these states, and approximate values of the dissociation energies calculated by the method of Birge and Sponer,[8] are given together with other information in Table III.

The present paper originated in the attempt to explain an important defect in the analogy to sodium, namely this: that the ^2P states are *inverted* for BO, CO^+, and CN, whereas the supposedly analogous ^2P state of sodium is *normal*. This discrepancy was first demonstrated in Jenkins' analysis of the structure of the BO α bands,[31] the proof depending on the numbers of "missing lines" in the $^2P_{1\ 1/2} \rightarrow {}^2S$ and $^2P_{1/2} \rightarrow {}^2S$ sub-bands. Examination of Baldet's data and photograph[32] for the λ3997 comet-tail band ($^2P \rightarrow {}^2S$) of CO^+ leaves little doubt that the same relation holds for CO^+. Unpublished work of Mr. Y. K. Roots and the writer on the red CN bands ($^2P \rightarrow {}^2S$) shows without question that the ^2P is also inverted in this case. Presumably the analogy extends also to the as yet undiscovered ^2P of N_2^+.

Interpretation of spectra, electronic quantum numbers and electron configurations: BO, CN, CO^+, N_2^+. There seems to be no possibility of accounting for an inverted ^2P state in terms of an electron configuration like that (closed shells *plus* one p electron) which gives the normal ^2P state of Na. The simplest assumption is that the inverted ^2P of BO, CO^+, and CN corresponds, like the inverted ^2P ground state of a halogen atom, to a configuration of closed shells *minus* one p electron (cf. Table I).[33] The missing p electron must in all probability be a $2p$ electron, since the number of electrons in the molecule is not large enough to give a shell of as many as three $3p$ electrons except in a highly excited state. Since the shell of six equivalent $2p$ electrons of an atom is subdivided in the molecule into two sub-shells

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(cf. pp. 194, 220), so that the assumption made here is justified only according as it is successful. *Possibly* our supposed l is merely n_s, and l itself is in general different, but unimportant.

[30] $\Delta l_\tau = \pm 3$ etc. will probably usually be weak because of rule 4 and for other reasons.

[31] F. A. Jenkins, Proc. Nat. Acad. Sci. **13**, 496 (1927).

[32] F. Baldet, Compt. Rend. **180**, 820, 1201 (1925).

[33] Other possible explanations, such as the assumption of incomplete shells of d or f, as well as of p electrons, are too improbable.

composed respectively of two $2s^p$ and four $2p^p$ electrons (cf. preceding section), it must be one of the latter which is missing in ^2P of BO.

In interpreting the three observed electron levels of BO, the fact that the combination $^2S \rightarrow {}^2P$ is much weaker[34] than $^2P \rightarrow {}^2S$ and $^2S \rightarrow {}^2S$ is also important. This indicates a strong tendency toward the validity of an additional selection principle besides $\Delta\sigma_l = 0, \pm 1$; it seems reasonable to identify this additional selection principle with the atomic rule $\Delta l_r = \pm 1$. This identification yields the conclusion that the united-atom quantum numbers l_r are approximately valid in these molecules. It also follows, if we exclude as improbable the presence of any electrons with $l_r > 2$, that the *emission electron* has $l_r = 1$ in the lower ^2S state, but $l_r = 0$ or 2 in the ^2P and in the upper ^2S state; or else $l_r = 0$ or 2 in the lower state and $l_r = 1$ in the two upper states.

Accepting the conclusions of the preceding paragraphs, we are led, as the simplest explanation of the observed relations, to the following electron configurations for the three observed states of each molecule; lower ^2S, $(A)(ms^p)^2(2p^p)^4(ns^x)$; ^2P, $(A)(ms^p)^2(2p^p)^3(ns^x)^2$; upper ^2S, $(A)(ms^p)(2p^p)^4(ns^x)^2$. Here A is an as yet undetermined closed-shell configuration of the six most firmly bound electrons, m and n are as yet undetermined principal quantum numbers, and x is s or d. The order in which the symbols ms^p, $2p^p$, and ns^x is written is intended to conform to the relative strength of binding of these types of electrons. The assignment given satisfies the following conditions: (1) $\sigma_l = 0, 1, 0, s = \frac{1}{2}$, for the states $^2S, {}^2P, {}^2S$, with $\Delta\sigma_l = 0$ or ± 1 in the observed transitions; (2) the ^2P is inverted; (3) the lower ^2S state has an outer configuration resembling that of unexcited Na; (4) $\Delta l_r = 1$ for the emitting electron in the strong transitions.

The energy order of the three observed molecular states then indicates the order of ionization potentials for closed shells corresponding to the three orbit-types, ms^p, $2p^p$, and ns^x. Quite as noteworthy as the existence of these three different ionization potentials is the fact that the differences are so comparatively small. Also of interest is the fact that according to the present interpretation, the transitions between the observed states are of an X-ray rather than of an optical type.

The diamagnetic ^1S normal state of CO or N_2, obtained in each case by adding an electron to the ^2S normal state of the ion, then presumably has a configuration $(A)(ms^p)^2(2p^p)^4(ns^x)^2$, composed wholly of closed shells. The absence of a ^3S state of CO or N_2 lying below the lowest ^1S state is satisfactory evidence for the assumed closed shell $(ns^x)^2$ as against $(ns^x)(ns^y)$.[35]

The configuration (A) must be either $(1s^s)^2(2s^s)^2(2s^p)^2$, $(1s^s)^2(2s^p)^2(2s^s)^2$, or $(1s^s)^2(2s^s)^2(3s^s)^2$. The first two closed shells in any case are essentially unchanged K shells of the separate atoms. One of these must, however, for

[34] Cf. ref. 5, p. 497, footnote 43. This combination $^2S \rightarrow {}^2P$ is known to be weak in BO and CO^+, and has as yet not even been observed in CN or N_2^+.

[35] Evidence for a $(ns^x)^2$ shell in the excited states of CO^+ etc. is the fact that a large amount of energy is surely required to go from $(ns^x)^2$ to (ns^x) (ns^y) in CO and so doubtless in CO^+; for neutral CO shows *no* excited levels below 6 volts.

purposes of the Pauli principle be considered as having been promoted, doubtless to $(2s^s)^2$ or $(2s^p)^2$. The third closed shell must probably be derived from two $2s$ electrons of the separated atoms. No direct spectroscopic evidence concerning these shells appears to be available.

The ms^p electrons are doubtless either $2s^p$ or $3s^p$ electrons. The $2p^p$ electrons are probably unpromoted $2p$ electrons of the atoms. The most loosely bound, ns^x, electrons ($x=s$ or d) cannot be $2s^s$, since this shell is surely not the most loosely bound, and has been accounted for already as surely a part of (A). Most probably they are $3s^s$, or perhaps $3s^d$, electrons; or if (A) includes a group $(3s^s)^2$, they are probably either $3s^d$ or $4s^s$ electrons.

The two most likely possibilities for the normal state of CO and N_2 appear to be:

(1) $(A)(3s^p)^2(2p^p)^4(3s^s)^2$, with $(A)=(1s^s)^2(2s^p)^2(2s^s)^2$,[36]

(2) $(A)(2s^p)^2(2p^p)^4(3s^d \text{ or } 4s^s)^2$, with $(A)=(1s^s)^2(2s^s)^2(3s^s)^2$.

The fact that the ms^p shell is always more firmly bound than the $2p^p$ shell is in agreement with alternative (1) if the ms^p electrons are former $2s$ atomic electrons promoted to $3s^p$; or also with alternative (2) if they are unpromoted $2s^p$ electrons derived from $2p$, or perhaps sometimes from $2s$. The fact that the ms^p electrons always show strong positive energy-bonding-power indicates an unpromoted status and so favors the second alternative.[36a] But if this is correct, we might expect the $3s^p$ orbit, which is not yet present according to configuration (2), to be next in order of binding, or at least to be more firmly bound than the $3p^p$ and $3p^d$ orbits; whereas in the normal state of NO, with one more electron than CO, the most loosely bound electron is actually found to be in an orbit, presumably $3p^p$ or possibly $3p^d$ (see below), with $\sigma_{l\tau}=1$. Other arguments can be given on both sides,[36a] but on the whole, alternative (1) seems the more probable, and will be assumed, tentatively, in the following discussion. It may be, or is even probable, that this special assignment is incorrect, but the unambiguous identification of A, m, n, and x is not vital to the present discussion. It is possible also that the *same* identification should not be made for *all* molecules. A definite decision in regard to these points can probably be made only with the help of many new data on band structures. It should be said, however, that the known facts about the molecules considered below offer no contradiction to the assignments involved for A, m, n, x in configuration (1).

Interpretation of ionization potentials in N_2 *and* CO. The conclusions here reached have an interesting bearing on the interpretation of ionization potential and positive ray data. In the case of CO the following ionization potentials are known: 14.2 volts, ionization begins; 16.9 volts, appearance of CO^+ comet-tail bands ($^2P \rightarrow {}^2S$); 20.0 volts, excitation of negative Des-

[36] A likely alternative for (A) is, $(A)=(1s^s)^2\,(2s^s)^2\,(2s^p)^2$. The possibility $x=d$ instead of $x=s$ also appears not unlikely.

[36a] The fact that the $3s^p$ electrons act like unpromoted electrons is perhaps after all not inconsistent with alternative (1), for if the $2s^p$ electrons in (1) act essentially like $1s^s$ electrons, it may be that this permits the $3s^p$ electrons to act essentially like $3s^p$ electrons.

TABLE III. *Quantum number assignments.*

Molecule	Energy (volts)	State ($\Delta\nu$)	Numbers of outer electrons $2s^a$	$3s^b$	$2p^p$	$3s^s$	$3p^p$	$3s^d$	$3p^d$	Molecular Constants $r_e(A.U.)$	$\omega_e(\text{cm}^{-1})$	$\omega_e x$	Dissociation Energy (volts) D^v	D	Probable Products	Remarks
Li_2	0	^1S	2							{2}	—	—	{1.3}	{1.3}	Li (^2S), s^2; Li (^2S), s^2	[Not known; estimated]
LiF	0	^1S	2	2	4					—	—	—	—	—	$Li^+(^1S)$, s^2; $F^-(^1S)$, s^2p^6	[Not known; estimated (see text)]
BeO	0	^1S	2	2	4					1.33	1465	12.7	6.4	6.4	Uncertain (cf. text)	BeO bands
	2.62*	^1S	2	1	4	1				1.36	1354	8.9	5.2	7.8	Uncertain (cf. text)	BeO bands
																or reverse?
C_2	0	^3P	2	2	3	1				1.31	1630	11.7	7.0	7.0	$C(^3P)$, s^2p^2; $C(^3P)$, s^2p	Swan bands
	2.39*	^3P	2	1	3	2				1.27	1773	19.4	6.4	8.8	{$C(^3P, s^2p^2$; $C(^1D)$, s^2p}	Swan bands
BeF	0	{^2S}	{2	2	4	1	}			—	1253	10.2	4.8	4.8	Uncertain (cf. text)	BeF bands
	4.10*	{$^2P(35)$}	{2	2	4		1}			—	1156	8.4	4.9	9.0	Uncertain (cf. text)	BeF bands
BIIO	0	^2S	2	2	4	1				1.21	1874	11.7	9.3	9.3	$B(^2P)$, s^2p; $O(^3P)$, s^2p^3	$^2P \rightarrow {}^2S$ strong
	2.91*	$^2P_i(126)$	2	2	3	2				1.36	1249	10.6	4.6	7.5	$B(^2P)$, s^2 or s^2p; $O(^3P)$, s^2p^3 or s^2p^2	$^2S \rightarrow {}^2P$ weak
	5.30*	^2S	2	1	4	2				1.31	1270	10.1	5.0	10.3	$B(^2P)$, s^2p; $O(^3P)$, s^2p^3	$^2S \rightarrow {}^2S$ strong
CN	0	^2S	2	2	4	1				1.17	2056	13.8	9.5	9.5	$C(^3P)$, s^2p^2; $N(^4S)$, s^2p^2	$^2P \rightarrow {}^2S$ strong
	1.78*	$^2P_i(56)$	2	2	3	2				{1.23}	1729	13.5	6.8	8.6	$C(^3P)$, s^2p; $N(^4S)$, s^2p^2	$^2S \rightarrow {}^2P$ unknown
	3.18*	^2S	2	1	4	2				1.15	2144	21.3	6.7	9.9	$C(^3P)$, s^2p^2; $N(^3D)$, s^2p^2	$^2S \rightarrow {}^2S$ strong
N_2	0	$X = {}^1S$	2	2	4	2				—	2345	14.4	11.7	11.7	$N(^4S)$, s^2p^3; $N(^4S)$, s^2p^3	Known bands,[41]
	8.18*	$A = {}^3S$ (or ^3D?)	2	2	3	2	1			—	1446	13.9	3.7	11.9	$N(^4S)$, s^2p^3; $N(^2D)$, s^2p^3 (or N, ^4S, s^2p^2?)	$X \leftarrow\rightarrow a$,
	8.50*	$a = {}^1P$	2	2	4	1	1			—	1679	13.8	5.7[z]	14.2[z]	$N(^2D)$, s^2p^3; $N(^2D)$, s^4p^3	$D \rightarrow B$,
	9.35*+	$B = {}^3P_n$[70?]	2	2	4	1	1			1.21	1718	14.4	5.3	14.6	$N(^2D)$, s^2p^3; $N(^2D)$, s^2p^3 (or N, ^4S, s^2p^2?)	$C \rightarrow B, B \rightarrow A$; also the somewhat uncertain
	13.00*+	$C = {}^3P_n$ [55?]	2	1	4	2	1			1.15	2019	26.0	1.6[z]	14.6[z]	$N(^2D)$, s^2p^3; $N(^2P)$, s^2p^3 (or N, ^2D, s^2p^2?)	$b \rightarrow X$ and $c \rightarrow X$ systems with initials levels
	14.80*	$D = {}^3D$(small) or ^3S	{2	2	4	1		1(or $3d^d$?)}		—	>1718	—	>0	>14.8	—	probably at 12.80 and 12.88 volts respectively.
N_2^+	16.9+	^2S	2	2	4	1				1.12	2187	16.3	9.1	9.1	$N^+(^3P)$, s^2p^2; $N(^4S)$, s^2p^2	$^2P \rightarrow {}^2S$ unknown
	{17}	^2P_i	2	2	3	2				—	—	—	—	—	$N^+(^3P)$, s^2p; $N(^4S)$, s^2p^2	$^2S \rightarrow {}^2P$ unknown
	20.1*+	^2S	2	1	4	2				1.08	2392	22.8	8	11	$N^+(^3P)$, s^2p^2; $N(^2D)$, s^2p^2	$^2S \rightarrow {}^2S$ strong
	24+	^2S?	1	2	4	2				—	low?	—	—	>7	$N^+(^3P)$, s^2p; $N(^2D)$, s^4p^3	
	397*+	S?	One K electron removed							—	—	—	—	—	—	K absorption frequency, cf. Thibaud[40]
CO	0	$X = {}^1S$	2	2	4	2				1.15	2155	12.7	11.2	11.2	$C(^3P)$, s^2p or s^2p^2; $O(^3P)$, s^2p^3 or s^2p^2	Known bands[37], $X \leftarrow\rightarrow a(10)$; $X \rightarrow a'(1)$;
	5.98*	$a = {}^3P(93)$	2	2	4	1	1			—	1725	14.5	6.4	12.4	$C(^3P)$, s^2p^2; $O(^3P)$, s^2p^3	$X \leftarrow\rightarrow A$ (10,000); $X \leftarrow\rightarrow b$? (600); $b \rightarrow a$;
	7.14*	$a' = {}^3S$?	2	2	3	2	1			—	1173	9	4.6	11.9	Same as X	$X \leftarrow\rightarrow B$(4000); $B \rightarrow A$; $X \leftarrow\rightarrow C$ (110, 000);
	7.99*	$A = {}^1P$	2	2	4	1	1			1.24	1499	17.2	4.0	12.0	Same as a	$c \rightarrow a$; $X \leftarrow\rightarrow E$(100, 000); $X \rightarrow F$(800, 000);
	10.35*+	$b = {}^3S$	2	2	4	1		1		—	(2214?)		small	—	$C(^3P)$, s^2p^2 or s^2p; $O(^3P)$, s^2p^2 or s^2p^3	$X \rightarrow G$ (7,000,000 each). The numbers in
	10.73*+	$B = {}^1S$	2	2	4	1		1		1.12	2132	50	2.8	13.5	{Same as b}	parentheses are very rough estimates of
	11.35*	$C = {}^1S$								—	(2133)		—	—	Two excited atoms	relative intensities in *absorption* (Birge,
	11.37*+	$c = {}^3P$?	{2	1	4	2	1}			—	—	—	—	—	—	private communication). That states C
	11.46*	$E = {}^1S$	{2	2	3	2			1}	—	(2134)		—	—	Two excited atoms	and E are S states is indicated by the fact
	12.30*	$F = {}^1P$?	2	2	3	2		1		—	1914	19.8	0.6	12.9	Two excited atoms	that $X \leftarrow\rightarrow C$ and $X \leftarrow\rightarrow E$ probably have
	13.00*															P and R branches only (Birge, private
	13.12*	G														communication).
	13.24*															

CO^+	14.2^+	^2S	2	2	4	1			1.11	2197	15.2	9.8	9.8	$C^+(^2P)$, s^1p; $O(^2P)$, s^2p^3	$^2P \rightarrow {}^2S$ strong
	$16.7^{\bullet+}$	$^2P_i(126)$	2	2	3	2			1.25?	1550	14.1	7.1	9.6	$C^+(^2P)$, s^2 or s^1p; $O(^2P)$, s^2p^3 or s^1p^2	$^2S \rightarrow {}^2P$ weak
	$19.8^{\bullet+}$	^2S	2	1	4	2			1.17	1698	24.3	3.7	9.3	$C^+(^2P)$, s^1p; $O(^2P)$, s^2p^3	$^2S \rightarrow {}^2S$ strong
NO	0	$X = {}^2P_n(124)$	2	2	4	2	1		1.15	1892	14.4	7.9	7.9	$N(^4S)$, s^2p^3; $O(^3P)$, s^2p^4	Known bands, $X \leftrightarrow A(5)$; $X \leftrightarrow B(1)$; $X \leftrightarrow C(30)$; $X \leftrightarrow D(20)$. The numbers in parentheses give approximate intensities in absorption.[47]
	$5.45^\bullet$	$A = {}^2S$	2	2	4	2		1	1.07	2352	13—	14	19.	(cf. text under NO, p. 210)	
	$5.60^\bullet$	$B = {}^2P_n(33)$	2	2	4	2		1	1.42	1030	7.5	4.4	10.	$N(^2D)$, s^2p^3; $O(^3P)$, s^2p^4	
	$6.45^\bullet$	$C = {}^2S$?	2	2	4	2(also one excited)			—	(2347)		—	—	—	
	$6.58^\bullet$	D	2	2	4	2(also one excited)			—	2324	27	6.2	13.	—	
NO^+	9.4^+	^1S?	2	2	4	2			—	—	—	—	—	$N(^4S)$, s^2p^3; $O^+(^4S)$, s^2p^2	
	21^+	^3S?	2	2	3	2	1		—	—	—	—	—	$N(^4(S)$, s^2p^3; $O^+(^4S)$, s^2p^2	
	22^+	P?	2	2	4	1	1		—	—	—	—	—	$N^+(^3P)$, s^2p^2; $O(^3P)$, s^2p^4	
O_2	0	$X = {}^3S$	2	2	4	2	2		1.21	1565	11.4	6.65	6.65	$O(^3P)$, s^2p^3; $O(^3P)$, s^2p^4	Known bands, $X \rightarrow A$ (atmospheric absorption bands) and $X \leftarrow\rightarrow B$ (Schumann-Runge bands)
	1.62•	$A = {}^1S$, ^1D?	{2	2	4	2	2}		1.23	1415	11.9	4.4	6.1	{the same}	
	6.09•	$B = {}^3S$	2	2	4	2	1	1	1.61	708	12.4	0.96[x]	7.05[x]	$O(^3P)$, s^2p^3; $O(^3P)$, s^2p^4	
O_2^+	13.5^+	$^2P_n(>200)$	2	2	4	2	1		—	1926?	16.5	6.9	6.9	$O^+(^4S)$, s^2p^2; $O(^3P)$, s^2p^4	Ultraviolet O_2^+ bands; cf. Table IV, note (*b*).
	{18.7•}	^2P_n	2	2	4	2		1	—	855	13.7	1.8	6.95	$O^+(^2D)$, s^2p^2; $O(^3P)$, s^2p^4 (? see text)	
	{18.7•}	{P?}	{2	2	3	2	2}		—	1026	11.1	2.9	{8.1}	$\{O^+(^4S); O(^3P)\}$	Visible O_2^+ bands
	{20.8+}	{S}	2	2	4	1	2		—	1180	17.8	2.4	{9.7}	One atom excited	
	524•	S?	One K electron removed						—	—	—	—	—	—	K absorption frequency, cf. Thibaud.[40]
F_2	0	^1S	2	2	4	2	4		{1.5?	1170	10	3.1	3.1}	$F(^2P)$, S^0P^3; $F(^2P)$, S^0P^3	All numerical values are estimates by Birge (cf. Table IV).
	{2.9}	^1S	2	2	4	2	3	1	{ —	320	18	0.2	3.1}	$F(^2P)$; S^0P^3; $F(^2P)$, S^0P^3	

Notes for Table III. General: (1) References to the sources of most of the numerical data for the various molecules will be found under the discussion of these molecules in the text. Free use has also been made in preparing Table III of Birge's very valuable compilation of molecular constants in *International Critical Tables*, cf. also R. T. Birge, pp. 230–2 of the National Research Council Report on Molecular Spectra. The writer is very greatly indebted to Professor Birge for the use of the International Critical Table material before publication. (2) Material cenclosed in { } in Table III is especially uncertain or speculative.

Special Notes: (3) The values given under "Energy (volts)" are all measured upward from the lowest known state of the neutral molecule assumed as zero. In most cases the lowest known state is known to be, or else is probably, the normal state (cf. text, and ref. 3, etc., for evidence). For ionized molecules the energy is also referred to the normal state of the neutral molecule as zero. The symbol • indicates that the value given has been obtained from spectroscopic data, while + indicates that it comes from excitation potential data. When both • and + are used, the *numerical* value given is, if possible, the spectroscopic value. In some cases, in particular N_2 and O_2^+, the values given depend on both spectroscopic and excitation potential data. (4) Under "State ($\Delta\nu$)" the known or probable molecular electronic state (often preceded by an empirical designation as given by Birge) is given; and, also, in the case of multiple states, the over-all multiplet width $\Delta\nu$. The subscripts *n* and *i* in such cases as ^1P_n, ^3P_i, etc., indicate respectively a *normal* or *inverted* multiplet; if no subscript is given, evidence is lacking as to the true designation. Only in the cases of CN, BO, CO^+, and N_2^+ and the states *X*, *A*, *B* of CO and NO are we *certain*, from analysis of band structure, that the state designations given (such as ^2P_i, ^2S, ^1P) are correct. In all other cases, the band analysis is incomplete, and the designations given are only *probable* (strictly, the ^2P_i state of CO^+ is also not yet certain). The value $\Delta\nu \backsim 70$ for the *B* level of N_2 is estimated from the $B \rightarrow A$ and $D \rightarrow B$ bands, assuming $\Delta\nu \lesssim 0$ for the *A* and *D* levels; the results from the $B \rightarrow A$ and the $D \rightarrow B$ bands are in good agreement. The value $\Delta\nu \backsim 55$ then follows if the $C \rightarrow B$ bands are $^2P_n \rightarrow {}^2P_n$, as seems probable. For the *a* level of CO, $\Delta\nu \backsim 93$ is estimated from the $a \rightarrow X$ and the $b \rightarrow a$ bands. (5) Under "Numbers of Outer Electrons" the probable, or most plausible, number of electrons of each of the types indicated is given, in accordance with the evidence of the present paper. As has been remarked elsewhere, it is likely that some of the orbit-types are not correctly designated (e.g. "$3s^{q}$" should perhaps be $4s^q$). In *all* cases, it is assumed that two of the first four electrons are bound in ($1s^q$) orbits, and two in $2s^p$ orbits. *In every case*, except apparently one state of O_2^+ (cf. Note 8 below), *the assignments given are such as to fulfill*, so far as known, *all the requirements stated under "Working Rules."* (6) The values given under "Molecular Constants" are mainly from Birge's compilation in International Critical Tables. The values for BeF are as given by Mecke (Zeits. f. Physik, 42, 412, 1927). (7) The dissociation energies D^0 and D are for the most part from Birge and Sponer[8] or from Birge (Int. Crit. Tables). D^0 refers to the (purely vibrational) energy of dissociation of the non-vibrating molecule in the stated (usually excited) electronic state, D to the *total* energy required to excite an electron (cf. second column of the table) and dissociate the molecule, starting from the normal state of the latter. *Most of the D^0 values* are obtained by a linear extrapolation from the lower vibrational levels[5] (i.e. we assume $D^0 = \omega_e^2/4\omega_e x_e$, in cm^{-1}, the result then being converted to volts), and for this reason *are probably only very roughly correct*: cf. ref. 8, also R. Mecke, *l.c.*; in a few cases, marked x, the results were obtained by a non-linear extrapolation and are probably too small,—except in the case of O_2 where the result should be very accurate since the vibrational levels were followed to the point of dissociation. (8) Under "Dissociation, Probable Products" are given the results which seem most likely from the discussion in the text in Part II. The state of each atom or ion is given according to the ordinary atomic classification, then the strong-field component of this atomic state necessary to give the molecular state in question (cf. Table II) is (partially) indicated by giving its σ_{lr} classification according to the system explained in the text preceding Table II. In all cases with the apparent exception of the initial ^2P state of the ultraviolet O_2^+ bands, and of the ^1S states of F_2 (cf. Part II), the molecular σ_{lr} configuration appears to be obtainable in the expected way as the sum of the atomic configurations: e.g. $N(^4S)$, s^2p^3; $O(^3P)$, s^2p^4 gives $NO(^2P)$, $s^{10}p^6$. For some of the N_2 levels, two possibilities are given in Table III for the dissociation products; the first of these corresponds to $D_x = 9.5$, the second and perhaps more probable (although indicated by "or . . . . ?") to $D_x = 11.8$ volts.

landres bands ($^2S \rightarrow {}^2S$) of CO^+.[37] According to the present interpretation, these three potentials respectively correspond to the removal of a $3s^\sigma$, a $2p^\pi$, and a $3s^\pi$ electron from the CO molecule. Thus in the production of the known states of CO^+ by electron impact, there is no need to assume simultaneous removal of one electron and excitation of another, a process which one would perhaps expect to be relatively improbable.

In nitrogen, ionization begins at 16.9 volts, and the negative bands ($^2S \rightarrow {}^2S$) are excited at 20.0 volts[38]; probably the expected $^2P \rightarrow {}^2S$ bands fall in the infra-red, from which it would follow that the ^2P ionization potential lies not far from 17 volts.

At 24 volts in nitrogen, there is another ionization potential, according to Smyth, and Hogness and Lunn.[39] This must correspond to the removal of an electron from the shell which we have designated as $(2s^\sigma)^2$, since the other three outer shells have already been accounted for, and since the ionization potential for the two most firmly bound shells is 397 volts (see below). Removal of this electron should give a ^2S molecule. Hogness and Lunn's work yields the information that, while N_2^+ is the primary ionic product both at 16.9 and at 24 volts, the N_2^+ ions formed below 24 volts are all of a stable character, while the 24 volt kind are decomposed, if enough opportunity is given for collisions, into N^+ and N. Probably, as Birge and Sponer suggest,[8] the 24 volt "excited N_2^+ molecule represents sufficient energy to change N_2^+ into $N^+ + N$" in collisions of the second kind.

If the selection principle $\Delta l_\tau = \pm 1$ is applicable, 24 volt N_2^+ ions, when collisions do not intervene, should revert in two steps to stable N_2^+, the first step (which should occur in either of two ways) giving ultraviolet bands which are as yet unknown or unclassified.

Smyth has reported a sharp increase in N^+ ions at 350 to 400 volts.[39] This may be interpreted as corresponding to the removal of an electron from one of the two inner, or K, shells, $(1s^\sigma)^2$ and $(2s^\pi)^2$, of N_2; according to spectroscopic evidence (cf. following paragraph), this occurs at 397 volts. The formation of N^+ may have been brought about by some secondary

[37] Cf. R. T. Birge for discussion and bibliography of CO levels (Phys. Rev. **28**, 1157, 1926). Further, J. J. Hopfield and R. T. Birge, Phys. Rev. **29**, 922*A* (1927). The values for the a' level are revised according to a private communication from Professor Hopfield.

Duffendack and Fox (Science, **64**, 277, 1926), and Miss A. B. Hepburn (unpublished work) find that the Baldet-Johnson or combination bands ($^2S \rightarrow {}^2P$) of CO^+ appear at 22.9 volts. These bands should however, be excited at the same potential (20.0 volts) as the $^2S \rightarrow {}^2S$ bands. Possibly the bands observed by Duffendack and Fox and by Miss Hepburn at 22.9 volts represent a new system. The 22.9 volt potential might be analogous to the 24 volt potential in N_2 (see below), and should then correspond to removal of a $(2s^\sigma)$ electron.

[38] H.Sponer, Zeits. f. Physik, **34**, 622 (1925).

[39] H. D. Smyth, Proc. Roy. Soc. **104***A*, 121 (1923). T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 786 (1925).

G. P. Harnwell (Phys. Rev. **29**, 840, 1927) has obtained evidence that in mixtures of helium and nitrogen the action $He^+ + N_2 \rightarrow He + N_2^+$ occurs with the formation of N_2^+ ions which dissociate on collision. This result seems to prove that the 24 volt N_2 potential of Hogness and Lunn lies with certainty below 24.5 volts, the ionization potential of helium.

[40] J. Thibaud, Nature, March 3, 1928.

process; this apparently did not occur in Hogness and Lunn's apparatus, since they find no increase in N^+ at these potentials.

Far ultra-violet spectra. The fluorescent emission of the ordinary negative nitrogen bands ($^2S \rightarrow {}^2S$ of N_2^+), found by Oldenberg to result from the action of ultraviolet light of very short wave-length,[41] can now be explained as follows: a $3s^p$ electron is removed by light absorption, following which one of the outer, $3s^s$, electrons falls in to replace it, giving a line of the negative band spectrum. Again the assumption of simultaneous excitation of one electron and ionization of another is avoided.

Thibaud has recently photographed K absorption edges for N_2, O_2, and also carbon compounds. For N_2 the edge is at $\lambda 31.1$, corresponding to 397 volts; and in agreement with our expectation that the energies of the promoted and unpromoted K electrons should differ very little, only a single edge is found. The results for O_2 and carbon are similar; the edges occur at 524 and 284 volts respectively. Thibaud has also obtained the $K\alpha$ line in emission for B, C, N, O; it seems likely that this "line" really represents, under suitable experimental conditions, a superposition of several *band systems* corresponding to the dropping of any one of the outer electrons of a molecule into a vacant K position.

Quantum assignments for electron levels of NO. Before considering the numerous known excited electron levels of neutral CO and N_2, it will be helpful to treat certain other molecules, beginning with NO (cf. Table III). The unexcited state of NO is a *normal* (i.e., not inverted) ^2P.[6] The energy of dissociation, as well as the value of ω_0, is lower here than for the normal state of N_2 or CO. The ionization potential (9.4 volts) is much lower than the ionization potential for the $3s^s$ shell of CO or N_2 (14.2 and 16.9 volts respectively). It is also lower than for any electron in the N or the O atom, showing that the binding energy of the most loosely bound electron has been *decreased* in the formation of NO. The NO^+ ions formed at 9.4 volts are stable in collisions.[42] All these facts point to the following conclusion: NO has the same configuration of closed shells as N_2 and CO, but the additional, last bound, electron in NO goes into a $3p^v$ orbit with large promotion energy and a pronounced negative bonding power. In particular, the presence of a *single* $3p^v$ electron accounts for the observed, normal, ^2P state.

The four known excited levels of NO (energies 5.45–6.58 volts, cf. Table III) all combine with the lowest level. Probably all correspond to excitation of the outer, $3p^v$, electron, of NO.[43]

In the initial, unquestionably also normal, ^2P state of the β bands,[6] the low values of D^v and of ω_0 ($\omega_0 = 1030$, $r_0 = 1.418\ A$) indicate that the electron has been transferred to an orbit of very large promotion energy and strong negative bonding power, probably a $3p^d$, or perhaps a $4p^p$, orbit. The fact

[41] O. Oldenberg, Zeits. f. Physik, **38**, 370 (1926).

[42] T. R. Hogness and E. G. Lunn, Phys. Rev. **30**, 26 (1927).

[43] From energy and other considerations, it is improbable that deeper-lying electrons are excited, unless to form the group $(3p^v)^3$. This latter possibility is also improbable when the σ_l and ω_e values of the observed states are considered.

that this ^2P is normal, with a $\Delta\nu$ which is neither large nor very small ($\Delta\nu\sim33$, as compared with $\Delta\nu\sim124$ for the lowest, also ^2P, state), supports such designations as these. The only likely alternative would be the configuration $(A)(3s^p)^2(2p^p)^3(3s^s)^2(3p^v)^2$, to which would correspond several molecular states (^2F_i, ^2P_n, ^2P_i, ^4P_i, ^2P_n—cf. Table I), all of which, however, would be expected to have a large $\Delta\nu$ (larger than 124), arising mainly from the $(2p^p)^3$ group. Also, it seems rather probable that the displacement of a $2p^p$ electron to a $3p^v$ orbit would require more than 5.6 volts (cf. lowest states of CO and N_2 in Table III).

In the initial, ^2S, state of the γ bands,[44] ω_0 is as large ($\omega_0=2352$, $r_0=1.068$ A) as in N_2, and the heat of dissociation, although not accurately known, is very much larger than for the normal and excited ^2P states (cf. Table III). These facts indicate that one of the dissociation products has an electron in a 3-quantum orbit (as e.g., in the 12.0 volt 3 D state $(1s)^2(2s)^2(2p)^3(3d)$ of the O atom),[8] and that this electron may be present in the molecule as an *unpromoted* electron, perhaps $3s^d$, with zero or a moderate positive distance-bonding power. The initial states of the δ and ϵ bands[45, 46, 47] appear to be similar in nature to that of the γ bands; possibly the excited electron is in a $3d^d$, or in some four-quantum state.

The interpretation of the initial states of the β and γ bands, as having respectively a $3p^d$ and a $3s^d$ excited electron, conforms to the selection rule $\Delta l_r=\pm1$ if the outer $3p^v$ electron in the normal state of NO is in a $3p^p$ state.[49]

States of NO involving the displacement of a $3s^p$, $2p^p$ or a $3s^s$ electron are apparently not known spectroscopically. Two additional ionization potentials have however been observed by Hogness and Lunn[42]: (a) $NO\rightarrow O^+ + N + \epsilon$ at 21 ± 1 volts, and (b) $NO\rightarrow N^+ + O + \epsilon$ at 22 ± 1 volts. In each case, the atom and ion are very probably in their respective normal states: dissociation of NO into normal N and O requires about 7 or 8 volts, while ionization of normal O requires 13.56, of normal N, 14.48 volts; hence the calculated potential for process (a) is about 21 volts, for process (b), about 22 volts.[8] Probably process (a) involves the removal of a $2p^p$ electron from NO, process (b), of a $3s^s$ electron; reasons for these conclusions will be given in Part II.

Electronic states of O_2^+. Although their structure has not been analyzed in detail, there can be little doubt that the ultraviolet O_2^+ bands represent a

[44] An examination of Frl. Guillery's data (Zeits. f. Physik, **42**, 121, 1927) shows conclusively that this state can only be a ^2S state; if it were a case b ^2P or ^2D state (the latter as in CH λ4300), there would be more missing lines.

[45] Analyzed by Birge (private communication) from photographs by Leifson (Astrophys. J., **63**, 73, 1926). See also H. P. Knauss, Phys. Rev., May, 1928 (Abstract).

[46] The δ bands at least, according to recent photographs taken by Mr. W. F. C. Ferguson in this laboratory, are closely similar in apparent structure to the γ bands. Probably their initial state is ^2S.

[47] The δ and ϵ bands are more strongly absorbed than the β and γ bands; the respective absorption coefficients, as estimated from Leifson's photographs (ref. 45, Plate *IVc*), are roughly in the ratio $\gamma:\beta:\delta:\epsilon:=5:1:40:20$.

$^2P \rightarrow {}^2P$ transition.[48] It is probable that this is completely analogous to the NO β bands, and that the final, ^2P, state ($\omega_0 = 1860$) is the lowest state of O_2^+ and has the same electron configuration as the lowest state of NO.[49]

The nature of the visible O_2^+ bands is much more uncertain. According to Frerichs[50] and Mecke,[50] they are of a complicated type, with many branches; and are unrelated to the ultraviolet bands. They show $\Delta\nu$ intervals of the order of 50 cm^{-1}; according to Mecke, each band has at least four heads with about this spacing. So far as can be seen from Frerichs' data and photographs, however, the structure is of the type characteristic of $^2S \rightarrow {}^2P$ transitions; combination relations which hold for the two strong branches make it probable that the *initial* state is the S state. If there are several heads, as Mecke indicates, the probable interpretation is $^4S \rightarrow {}^4P_i$, but the two strong branches associated with the first head do not support this; the difficulties would be greater for ^4P_n. Either $^4S \rightarrow {}^4P_i$ or $^2S \rightarrow {}^2P_n$ can be reasonably interpreted in terms of the following initial and final electron configurations: $(A)(3s^p)^2(2p^p)^4(3s^s)(3p^p)^2$, ^4S or ^2S, $\rightarrow (A)(3s^p)^2(2p^p)^3(3s^s)^2(3p^p)^2$, ^4P_i or ^2P. These possible interpretations present the difficulty, in regard to the final state, that $\Delta\nu \sim 50$ (^2P) or even $\Delta\nu \sim 150$ (^4P_i, with four heads at intervals of 50 cm^{-1}), is smaller than would be expected; for in the final state configuration the missing $2p^p$ electron, which has a smaller n^* than the $3p^p$ electron responsible for $\Delta\nu$ of the unexcited ^2P state of O_2^+ ($\Delta\nu > 200$ cm^{-1}) should be mainly responsible for $\Delta\nu$ and should give a *large* $\Delta\nu$. A possible interpretation avoiding this difficulty is $(A)(3s^p)^2(2p^p)^4(3s^s)(3p^p)^2, {}^2S \rightarrow (A)(3s^p)^2(2p^p)^4(3s^s)^2(4p^p), {}^2P_n$; this involves a double electron jump, but of legitimate type ($\Delta l_1 = 0$, $\Delta l_2 = 1$). The question can be settled only by analysis of the bands. It will be noted that *all* the interpretations suggested involve an S initial state which would be obtained from the ^3S normal state of O_2 (see below) by removal of a $3s^s$ electron.

The existing data on ionization potentials of oxygen are difficult to reconcile with one another. Lockrow[51] finds that the ultraviolet bands begin to appear at about 19.2 volts, and the visible bands at about 21 volts. Since the ultraviolet bands involve an electron jump of at least 4.73, or more probably as much as 5.2 volts,[8] this would give about 14 volts for the minimum ionization potential of O_2. (Lockrow gives 16 volts, but apparently this is unreliable.) Mackay finds ionization potentials at 12.5 and 16.1 volts, Hogness and Lunn at 13 ± 1 volts, Smyth at 15.5 volts.[52,53,54]

[48] Cf. ref. 6, p. 174.

[49] The much larger observed doublet separation (200 cm^{-1} as compared with 92 for NO),—this represents the *difference* between the $\Delta\nu$'s of the final and initial ^2P states—is not surprising, since according to the Landé formula[15] $\Delta\nu$ increases rapidly with increased binding energy, and because the binding energy for the $3p^p$ electron must be considerably larger for O_2^+ than for NO (9.4 volts), since even for *neutral* O_2 it is 13 volts.

[50] R. Frerichs, Zeits. f. Physik, **35**, 683 (1926); R. Mecke, Zeits. f. Physik, **36**, 801 (1926).

[51] L. L. Lockrow, Astrophys. J. **63**, 205 (1926). The potential at 19.2 volts appears to be, as we should wish, that for the vibrationless initial state, according to Lockrow's data. The same appears to be true for the 21 volt potential.

[52] C. A. Mackay, Phys. Rev., **24**, 319 (1924).

We shall probably not be far wrong if we assume 13.5 volts as the lowest ionization potential, corresponding to the removal of a $3p^p$ electron from unexcited O_2 to give unexcited O_2^+. Using 5.2 volts for the electron jump in the ultraviolet bands, the excitation potential of these bands should then be 18.7 volts. This potential corresponds, according to the present interpretation, to the removal of a $3p^p$ electron from O_2 and simultaneous excitation of a second $3p^p$ electron to a $3p^d$ orbit.

Assuming Lockrow's *relative* potentials for the visible and ultraviolet bands to be correct, we then get 20.5 volts for the excitation of the visible bands, corresponding, according to the interpretation given above, to removal of a $3s^s$ electron from O_2. Since the electron jump in the visible bands corresponds to 2.0 volts, this gives 18.5 volts as the calculated potential for the *final* state of these bands. This then is the voltage required for removal of a $2p^p$ electron from O_2, if either of the first two of the three interpretations suggested above for the final state of the visible bands is correct.

If transitions occur between the final state of the visible bands and the normal state of O_2^+, the resulting bands must lie in the same spectral region as the known ultraviolet bands, for the initial energy is practically the same in both cases. Since no such bands have been found, we may conclude that they are absent, or at least very weak. A reason for this may be found in the fact that according to *any* of the electron configurations suggested above for the final state of the visible bands, the transition to the normal state would involve $\Delta l_\tau = 0$. It seems likely that Hund's characteristic selection rule for symmetrical molecules here finds expression in the *strict* exclusion of all electron jumps not conforming to the rule $\Delta l_\tau = \pm 1$. Further evidence for this same conclusion is found in the case of N_2 as discussed below.

According to Hogness and Lunn,[53] ionization of O_2 at 13 volts gives a form of O_2^+ which is stable in collisions, while at 20 volts another type of ionization sets in which gives directly $O^+ + O$; there is no evidence of unstable O_2^+ molecules which decompose on collision. Smyth[54] obtained similar results, except that he gives 15.5 and 23.0 volts, values which should presumably be corrected by about -2 volts. The 13 volt potential has already been discussed. Hogness and Lunn's 20 volt potential must be interpreted as corresponding to the formation of a state of O_2^+ whose ω_0 and heat of dissociation are very low, so that the probability is very strongly in favor, in addition to the removal of an electron, of simultaneous transfer of enough vibrational energy to produce dissociation.[8] This state of O_2^+ is presumably the initial, ^2P, state of the ultraviolet bands, since, of the known excited states of O_2^+, this one has much the lowest ω_0 and heat of dissociation. Furthermore, the potential 20.5 volts (assuming the corrections given in the third paragraph above) is almost exactly the extrapolated convergence limit of the vibrational levels associated with this state.[8]

The excited states of O_2^+ formed by the removal of a $2p^p$ electron (18.5 volts?) or a $3s^s$ electron (20.5 volts) are presumably stable even in collisions;

[53] T. R. Hogness and E. G. Lunn, Phys. Rev., **27**, 732 (1926).
[54] H. D. Smyth, Proc. Roy. Soc., **105***A*, 116 (1924).

the proximity of these potentials to the 20.5 volt dissociation potential is probably a coincidence. Removal of a $3s^p$ electron doubtless occurs not far above 20 volts, also giving a stable form of O_2^+.

Electron configurations of O_2 and F_2. A comparison of certain band systems of NO, O_2^+, O_2 and F_2 shows a striking parallelism together with a progressive change (cf. Table IV). Although no experimental values are directly available for the F_2 absorption bands, Birge has obtained estimates of the con-

TABLE IV.

Molecule	Bands Designation	Volts	Vibration frequencies ω_0''	$\omega_0''x''$	ω_0'	$\omega_0'x'$	Heats of dissociation (Volts) D''	D'
N_2	^1S		2345	14.4			11.8	
NO	$^2P\rightarrow{}^2P$	5.60	1892	14.4	1030	7.5	7.9	10?
O_2^+	$^2P\rightarrow{}^2P$	5.2?	1926?	16.5	855	13.7	6.9	6.95
O_2	$^3S\rightarrow{}^3S$	6.09	1565	11.4	708	13−	6.65	7.05
F_2	$^1S\rightarrow{}^1S$	[2.9]	[1170]	[10]	[320]	[18−]	[3.1]	[3.1]

Notes. (*a*) D' is the total energy required to excite and dissociate the molecule. (*b*) The values of D, ω_0'', and of the electronic energy, for O_2^+, assume that $n''=0$ of Birge and Sponer[8] is really $n''=2$ (n = vibrational quantum number). (*c*) The data for F_2 are estimated by Birge (Int. Crit. Tables).

stants for F_2 which cannot be far wrong. This is done by a systematic comparison of the analogies and progressive changes for the known bands of Cl_2-Br_2-I_2 and of O_2-S_2-Se_2-Te_2.

The relations shown in Table IV may reasonably be interpreted as follows. Let us consider first the normal states. N_2 and CO have higher heats of dissociation than any other neutral diatomic molecules. Leaving out of account the four K electrons, these molecules have each six unpromoted and four promoted electrons, giving a large net bonding effect. In NO, O_2, and F_2 we have one, two and four promoted $3p^p$ electrons outside the N_2 configuration; in F_2 we have a closed shell of such electrons, giving a ^1S state. Each added $3p^p$ electron has a negative effect on the bonding, so that ω_0 and the heat of dissociation steadily fall. In F_2, with six unpromoted and eight promoted electrons, the net bonding effect has become small, and with the resulting large r_0, the entire electron configuration approaches that of two separated atoms.

Two $3p^p$ electrons as in O_2 should give a ^3S, a ^1D and a ^1S molecular state (cf. Table I), and one of these (^3S if the order of levels is as in atoms) should be the normal state of O_2. A ^3S normal state is in agreement with the magnetic behavior of O_2.[55] Also, the ultraviolet Schumann-Runge absorption and emission bands (these are the bands of Table IV)[56] have a structure which can hardly be other than $^3S\rightarrow{}^3S$.[57] The interpretation of the atmospheric

[55] R. S. Mulliken, Phys. Rev., **28**, 505 (1926). J. H. Van Vleck, Nature, May 7, 1927; Phys. Rev., **31**, 608 (1928).

[56] Cf. Birge and Sponer, l.c. ref. 8, page 268, for bibliography and discussion.

[57] These bands, according to data of Runge (Physica, **1**, 254, 1921) consist apparently of P and R branches only. This must be interpreted in the sense that $\Delta j_k=\pm 1$ rather than

absorption bands (cf. Table III) is, however, a puzzle; these bands do not obviously correspond to any expected structure type.[58]

Granting that in the emission of the NOβ bands an electron goes from a $3p^d$ to a $3p^p$ orbit, we may reasonably assume that the same thing happens for the analogous bands of O_2^+, O_2 and F_2 in Table IV. A transition $3p^d \rightarrow 3p^p$ of the emitting electron is in harmony with the respective transitions $^2P \rightarrow {}^2P$, $^3S \rightarrow {}^3S$, $^1S \rightarrow {}^1S$ for the molecule as a whole in NO, O_2, and F_2. It also satisfies the rule $\Delta l_r = 1$, which apparently holds strictly for symmetrical molecules.

Molecules C_2, BeF, BeO, LiF. Turning now to molecules with *fewer* electrons than CO, CN, and the like, let us consider C_2, the emitter of the Swan bands ($^3P \rightarrow {}^3P$).[59] The final, very likely unexcited,[60] ^3P state may reasonably be interpreted as $(A)(3s^p)^2(2p^p)^3(3s^s)$, the initial ^3P state as $(A)(3s^p)(2p^p)^3(3s^s)^2$. Both should then be inverted; whether this is the case is not yet known experimentally. The "high pressure carbon bands" perhaps represent the corresponding $^1P \rightarrow {}^1P$ transition.

The normal state of BeF may be ^2S like that of BO, but the excited ^2P state, if it is such, probably has $\Delta\nu \sim 35$ as compared with 126 for BO, and can hardly be analogous to the ^2P state of BO. But the structure of these bands is as yet doubtful.

The lowest known state of BeO is ^1S, and may, together with the normal state of LiF, be $(A)(3s^p)^2(2p^p)^4$.

Excited levels and selection rules in nitrogen and carbon monoxide. The very stable molecules N_2 and CO are the only molecules, other than H_2 and He_2, for which a considerable number of electron states is known. The configuration $(A)(3s^p)^2(2p^p)^4(3s^s)^2$ of the normal states of these molecules —cf. above—precludes the occurrence of any bands in the visible and near ultraviolet analogous to those of BO, CN, CO^+ and N_2^+. Excited states of CO and N_2 must then be obtained by displacement of an electron to a higher orbit, such as one of the orbits $3p^p$, $3p^d$, and $3s^d$ which are revealed by NO. By a consideration of the promotion, bonding and energy level properties of various orbits, as deduced from the molecules already discussed, a plausible

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$\Delta j = \pm 1$ (cf. R. S. Mulliken, Phys. Rev., **30**, 138, 1927). To avoid quarter-integral quantum numbers and a rule $\Delta j_k = \pm 1/2$, alternate lines must be assumed missing. The lines which remain are however *double*, the components becoming more nearly equal in intensity with increasing j, but not by any means approaching an asymptotic equality in this respect. If we assume that the stronger doublet component is itself an unresolved double, we have here exactly the predicted structure for a $^3S \rightarrow {}^3S$ transition in a symmetrical molecule.

(Added in proof). In a recent paper (Zeits, f. Physik, **49**, 167, 1928), W. Ossenbrüggen has shown definitely that the Schumann-Runge system consists of P and R branches, with integral rotational quantum numbers (evidently j_k): $j_k' = 0, 2, 4, \cdots$, $j_k'' = 1, 3, 5, \cdots$, $\epsilon' = Bj_k(j_k+1)$. He does not discuss the fine structure of the band lines.

[58] Possibly they involve absorption from ^3S to the expected metastable ^1D and ^1S states; this would accord with the fact that they are only moderately absorbed in the passage of sunlight through the whole thickness of the earth's atmosphere.

[59] For bibliography cf. J. D. Shea, Phys. Rev., **30**, 825 (1927) and W. E. Pretty, Proc. Phys. Soc. (London), **40**, Part 3,71 1928.

[60] According to T. Hori (Nature, July 3, 1926), the Swan bands are obtained in absorption in certain explosion spectra.

assignment of configurations has been made for a number of the excited states.[61] This assignment is given in Table III.

Hund's selection rule for symmetrical molecules, requiring that for any three electron levels not more than two electron transitions shall occur, shows no exceptions in the case of N_2. Thus none of the transitions $D \rightarrow A$, $C \rightarrow A$, $c \rightarrow a$, $b \rightarrow a$, all of which would fall in the near ultraviolet, have ever been observed. Transitions $X \rightarrow A$, $X \rightarrow C$, and $X \rightarrow D$ are not recorded in the far ultraviolet absorption or emission spectra of nitrogen, investigated by Birge and Hopfield, and Sponer.[62] Every transition mentioned is one which *should* be absent according to Hund's selection principle. The only expected transition involving known levels of N_2 which has not yet been observed is $B \rightarrow X$, which should be of low intensity on account of $\Delta s = 1$. For the known levels of N_2,[61] Hund's selection principle can apparently be expressed in the form $\Delta l_r = \pm 1$, so that it is equivalent to a sharpening of the principle which holds for the *strong* transitions in BO and CO^+ and probably CO; in regard to the theoretical justification of this form, cf. the section above on *Working Rules*.

If the assignments given in each case are correct, the same selection principle $\Delta l_r = \pm 1$ is obeyed in all the known bands of N_2^+, O_2^+, O_2, and F_2, while bands which would conflict with this rule are unknown (cf. discussion under O_2^+). The apparent absence of the "combination bands" $^2S \rightarrow {}^2P$ in N_2^+ may be ascribed to this cause.

The CO molecule possesses a richness of band systems which shows very clearly the absence of a strict selection rule like that in N_2. Transitions

[61] Hopfield has recently reported four new systems of nitrogen bands (Abstract 89, Washington meeting Am. Phys. Soc., April, 1928; and additional details very kindly given the writer by Professor Hopfield). The electronic energies correspond approximately to 7.09 volts (0, 0 band of strong series), 7.15 volts (0, 0 of strong series), 8.14 volts (single strong band), 8.61 volts (single weak band). All the bands, except perhaps that at 8.61 volts, are so diffuse that they must be ascribed to a polyatomic form of nitrogen, or if to N_2, must involve a multiple upper level (^3P or ^3D).

The latter alternative seems very improbable, since an inter-system combination such as $^1S \rightarrow {}^3P$, starting from the ^1S normal state of N_2, should be weak (cf. $X \rightarrow a$ of CO, Table III), while three of the above four band systems are strong (about of the same intensity on Hopfield's plates as the familiar $X \rightarrow a$, probably $^1S \rightarrow {}^1P$, bands of N_2). Also, the extrapolated convergence limit of both the 7.09 and the 7.15 volt systems comes at about 9.1 volts; since, however, a ^3P or a ^3D N_2 molecule cannot dissociate into two unexcited N atoms (cf. Table II and accompanying discussion) but must give at least one excited atom, excited at least as far as the ^2D state (2.39 volts), the heat of dissociation D of N_2 cannot exceed $9.1 - 2.39 = 6.7$ volts if the bands are due to N_2. Although there is evidence, that D is lower than the value 11.4 volts given by Birge and Sponer, it seems very improbable that it is as low as 6.7 volts.

For the above and several other reasons, it seems to the writer very improbable that Hopfield's new bands are N_2 bands, in spite of the fact that Hopfield finds that they cannot be ascribed to any familiar impurity. Apparently they must be attributed to polyatomic molecules formed in the preparation of the nitrogen, which was obtained by explosion of NaN_3.

[62] Cf. H. Sponer, Proc. Nat. Acad. Sci., **13**, 100 (1927); J. J. Hopfield, and Birge and Hopfield, Phys. Rev., **29**, 356*A*, 1927. Also, Prof. Birge informs the writer that the absence of far ultraviolet N_2 bands in the spectrum of active nitrogen has again been verified in work of H. P. Knauss.

between the normal level and almost every known excited level occur. According to the assignments in Table III, the levels a, a', and A of CO are ^3P, ^3S, and ^1P and are respectively analogous to B, A, and a of N_2.

From Table III it will be seen that while the supposed analogy of CO to Mg is for the most part not very close, there still remains a good analogy between the three levels X, a, and A, and the three lowest levels, ^1S, ^3P, and ^1P of Mg. Except for the unexplained reversal of the energy order of ^3P and ^1P, a similar statement is true for levels X, B, and a of N_2.

Active nitrogen. Absence of intersystem combinations in N_2. According to the assignments here given, and the selection rule $\Delta l_r = \pm 1$, the lower vibrational levels of the lowest known excited state of N_2 (the "A" level, a ^3S or ^3D level lying at about 8.2 volts) are truly metastable.[63] For the higher vibrational levels of the A state, however, transitions should occur to vibrational levels belonging to the B electron state (^3P), which lies at 9.35 volts, and thence back to lower vibrational levels of the A state. This is in agreement with conclusions reached by various people[64] that active nitrogen contains metastable molecules which are able to transfer to other molecules amounts of energy up to but usually not much exceeding 9.4 volts. It is also in accord with Sponer's failure to obtain any far ultraviolet emission bands from active nitrogen even with exposures of sixty hours.[62]

There is, however, a difficulty: why do not a large fraction of the vibrating molecules of level A make transitions to level a which lies at 8.5 volts, and then go immediately to the normal state with emission of the known $a \rightarrow X$ bands? This transition $A \rightarrow a (^3S \text{ or } ^3D \rightarrow ^1P)$ is not excluded by the selection rule $\Delta l_r = \pm 1$, and would be expected to proceed sufficiently fast (in spite of $\Delta s = 1$) to remove effectively the metastablity of the A levels above 8.50 volts. From the evidence just cited in regard to active nitrogen, including Sponer's results, it seems clear that this does not occur. Although no theoretical reason for doing so is evident, it seems almost necessary to conclude that in symmetrical molecules such as N_2, transitions involving $\Delta s = 1$ are *strictly* ruled out.[61] This conclusion is also supported by the absence, in Sponer's work and in that of Birge and Hopfield,[62] of the transition $B \rightarrow X (^3P \rightarrow ^1S)$, which is not excluded by the $\Delta l_r = \pm 1$ rule.

[63] According to experiments of Levesley (Trans. Faraday Soc., **23**, 552, 1927), N_2 has also a critical potential at 6.3 volts. If such a level exists, it must be metastable (possibly ^3D) since no bands are known going from it to the normal state.

[64] R. T. Birge, cf. H. P. Knauss, Phys. Rev., May, 1928 (abstract). Cf. also B. Lewis, Journ. Am. Chem. Soc., **50**, 27 (1928). Okubo and Hamada, Phil. Mag. (7) **5**, 372 (1928); P. A. Constantinides, Phys. Rev. **30**, 95 (1927); J. C. McLennan, Nature, April, 1928; Ruark and co-workers (J. Opt. Soc. Am. **14**, 17, 1927) and the present writer (Phys. Rev., **26**, 28, 1925) found evidence that active nitrogen can transfer amounts of energy as large as 10 or 10.4 volts. Perhaps the limitation to 9.4 volts holds only for low pressures where the metastable molecules alone survive long enough to make collisions. At higher pressures non-metastable ^3P molecules with energies as high as 11.4 volts, and also 3-body collisions involving two N atoms, may become important.

[65] R. Mecke, Naturwiss., **13**, 698 (1925); Zeits. f. Physik, **36**, 797 (1926).

APPENDIX. Derivation of results of Table I

The possible molecular *states* for the various *electron configurations* of Table I can be determined by means of the Pauli principle (cf. ref. 15, p. 115). This is done by Pauli's method of imagining the atom in an external magnetic field so strong that all couplings between electrons are broken down, so that each electron can be given four quantum numbers, n, l, m_l, and m_s. In a molecule, this breaking down is partly accomplished by the intramolecular electric field. But as compared with a strong magnetic field, a strong electric field shows two peculiarities, (a) unlike the magnetic case, states differing only in the sign of σ_l do not differ in energy, (b) an electric field has no action on the electron spins, hence has no power to orient the latter, nor to break down any couplings which may exist between spins of different electrons; if $\sigma_l > 0$, however, the spin is oriented with repect to σ_l,[9] hence indirectly with respect to the electric axis. We shall temporarily assume a supplementary magnetic field parallel to the electric axis so that n, l, m_l, and m_s can be specified for each electron. We shall use m_l and m ($m = m_l + m_s$) here so long as the magnetic field is supposed present, but σ_l and σ ($\sigma_l = |m_l|$ and $\sigma = |m|$) for the undisturbed molecules. (In the body of the paper, this distinction is dropped, σ_l being used at times with a + or − sign.)

In order to determine the possible molecular states for a particular electron configuration, such as for example one composed of two electrons with $n_\tau = 2$ and specified values of l_τ and $\sigma_{l\tau}$, we first write down all the possible combinations of m_l and m_s values which are compatible with the given configuration and which also satisfy the Pauli principle. This is done in Table V for *all* the possible configurations, namely $(2s^s)^2$, $(2s^s)(2s^p)$, $(2s^p)^2$, $(2s^s)(2p^p)$, $(2s^p)(2p^p)$ and $(2p^p)^2$, which can be obtained from two 2-quantum electrons. In Table V, in the columns headed "Possible Electron States," a + sign is used to indicate the presence of an electron with $m_s = +\frac{1}{2}$, and of type (in respect to l and m_l) specified at the head of the column, while a − sign indicates the presence of an electron with $m_s = -\frac{1}{2}$. In the succeeding columns under "Resultant" are given the resultant m_l, m_s, and m values obtained by addition, and the s values (always $s \geqq |m_s|$) deduced by a consideration of the grouping of the individual components into multiplets. The resulting molecular states (single states or multiplet components as the case may be) are given in the column under "Molecular State." The superscript letters, and the column "Atomic State" are not important for present purposes; they will be explained later.

In determining s values and "molecular states" we note that on removal of the assumed magnetic field, leaving only the characteristic intramolecular axial electric field, some of the magnetic field components fall together in groups of two or three, while at the same time a coupling of individual spins to give the resultant s asserts itself. Quantum numbers whose existence depends on the magnetic field are indicated in Table V by

TABLE V. *Possible electron distributions and molecular states for two 2-quantum electrons.*

Possible Electron States				Resultant				Molecular state	Atomic state
$2s^s$	$2s^p$	$2p^p$							
$m_{l_T}=0$	0	+1	−1	m_l	m_s	m	s		
(+)(−)				0	0	0	0	$^1S^S$	^1S
(+)	(+)			0	(+1)	(+1)	1	$^3S^P$	
(+)	(−)			0	0	0	0 and 1	and	
(−)	(+)			0	0	0			
(−)	(−)			0	(−1)	(−1)	1	$^1S^P$	^3P
+		+	−	±1	±1	±2	1	$^3P_2{}^P$	and
−									
+		−	+	±1	0	±1	0 and 1	$^3P_1{}^P$ and $^1P^P$	^1P
−				±1	0	±1			
−		+	−						
+									
−		−	+	±1	±1	±0	1	$^3P_0{}^P$	
+									
	+	+	−	±1	±1	±2	1	$^3P_2{}^P$	
	−								
	+	−	+	±1	0	±1	0 and 1	$^3P_1{}^P$ and $^1P^D$	^3P,
	−								
	−	+	−	±1	0	±1			
	+								
	−	−	+	±1	∓1	±0	1	$^3P_0{}^P$	^1S(?)
	+								
		(+)	(+)	0	(+1)	(+1)	1	$^3S^P$ and	and
		(+)	(−)	0	0	0	0 and	$^1S^S$	part of
		(−)	(+)	0	0	0	1	(or $^1S^D$?)	^1D
		(−)	(−)	0	(−1)	(−1)	1		
(+)	(−)			0	0	0	0	$^1S^D$ (or $^1S^S$?)	part of
		+−	+−	±2	0	±2	0	$^1D^D$	^1D (and ^1S?)

parentheses. In more detail, the relations which exist in this process are as follows:

(a) if $\sigma_l > 0$, each pair of configurations which differ only in respect to the sign of m_l and *simultaneously* of m, falls together, giving a single molecular state. [This state has, however, a double statistical weight and is capable of splitting again into two states when the molecule rotates (σ-type doubling[66]).] In describing such a state, one uses a symbol, such as $^3P_2$ to indicate $\sigma_l=1$, $\sigma=2$, $s=1$; a quantum number σ_s may also be defined, such that $\sigma=\sigma_l+\sigma_s$; σ_s, unlike σ_l and σ, is allowed to have both positive and negative values.[67]

(b) if $\sigma_l=0$, there is nothing to orient the spins on withdrawal of the magnetic field. Consider for example a ^3S state as in Table V. This gives

[66] Empirical relations, cf. R. S. Mulliken, Phys. Rev., **28**, 1202 (1926); **29**, 391, 637 (1927); **30**, 785 (1927); E. Hulthén, Zeits. f. Physik **46**, 349 (1927).

Theory, F. Hund[9,11]; R. de L. Kronig, Zeits. f. Physik, **46**, 814 (1928).

[67] When the nuclear rotation is considered, the coupling of σ_l and s tends to break down so that σ_s and σ lose their meaning (Hund's case *b*), but an adiabatic correlation with this case can be given.[9] Cf. F. Hund[9] and R. S. Mulliken (Phys. Rev., **29**, 637 (1927)) for discussion of the quantum numbers σ, σ_l, σ_s.

three magnetic components with $m=m_s=+1,0$, and -1, which fall together on removal of the field, giving a single state. [This, however, has triple weight, and in the actual molecule usually splits again into three when the molecule rotates[68].]

(c) In the ^3S case just discussed, it is evident that the values $m_s=+1,0$, and -1 may be regarded as the three possible m_s values corresponding to a resultant spin $s=1$. As will be seen in Table V, there are (for example) four $(2s^s)(2s^p)$ strong-field configurations, three of which unite to ^3S; the fourth, with $m_s=0$, must then evidently represent a ^1S state. Similarly in cases where $\sigma_l>0$, the proper s values can readily be picked out, always in such a way that the resulting molecular multiplets (such as ^3P) correspond to the correct number of magnetic components.

Since it cannot be assumed that the quantum numbers here used correspond, even approximately, in general, to those actually appropriate for a particular molecule, it is desirable to see what the results of Table V mean in terms of other quantum numbers. In case the quantum numbers l_r used here have a real physical meaning, they must have a tendency to give a resultant l, as in atoms. In an adiabatic transition to an imagined case where this tendency is realized, the individual σ_{l_r}'s would lose their significane, but σ_l, σ_s, σ and s should persist through all stages.

One can proceed further, to the united atom. As the nuclei come nearer, the (l, s) couplings should finally become important, giving j values; in this process σ remains to the last, but σ_l and σ_s disappear, giving place to σ_j. Finally for the united atom we have only n_r, l_r, l, s, and j. The set of molecular states given, taken as a whole, should in the above process go over with certainty into the set of atomic states listed in the last column of Table V, so long as similar states with different values of n do not come too near. A *possible* correlation of the *individual* molecular states with the individual atomic states is that indicated in the table. This correlation corresponds to that expected for an ordinary atom on withdrawal of a strong electric field, as determined by methods such as are used in the application of the Pauli principle in atoms.[15] One cannot however expect in general to find this particular correlation in actual molecules. For example, we know that the various electric field components of a ^3P atomic state must be correlated with an equal number of components belonging to a ^3S molecular state and a ^3P molecular state. But when as here there are two ^3P atomic states, it might happen that *each* derives some components from one molecular ^3S or ^3P state, others from the other. Such a mixed correlation would be conditioned mainly by an overlapping of energy levels of different molecular states at some stage of approach of the nuclei. Such overlapping, or even complete revolution in the order of levels, may be expected if a tendency toward separability in elliptical coordinates (cf. following paragraphs) becomes dominant. Overlapping of sets of levels

[68] Cf. F. Hund [9,11].

differing in n is often also to be expected, especially in view of the phenomenon of promotion of electrons.

Going back now to the n_τ, l_τ, $\sigma_{l\tau}$, s, σ_s assignment, we may next inquire what happens if the intramolecular electric field is so strong as to break down completely the ordinary l quantization. This condition is to be definitely expected in the case of non-penetrating orbits. Such a situation gives some degree of approach to quantization in elliptical coordinates (very close, for H_2^+). *The category of molecular states, as given in Table V, remains unchanged in elliptical coordinates.* Table V also holds for the individual field components, if we merely re-interpret the designations $2s^s$, $2s^p$, $2p^p$. In the *spherical* coordinates assumed in Table V, using the lowered quantum number values natural in the new quantum mechanics, $2s^s$ means $n_r=1$, $n_\theta=0$, $n_\phi=0$, $2s^p$ means $n_r=0$, $n_\theta=1$, $n_\phi=0$, $2p^p$ means $n_r=0$, $n_\theta=0$, $n_\phi=\pm1$, where $n=n_r+n_\theta+|n_\phi|+1$, $n_\theta+|n_\phi|=l$, and n_ϕ means the same as $m_{l\tau}$ of Table V. In *elliptical* coordinates, we might have $2s^s$ meaning $n_\xi=1$, $n_\eta=0$, $n_\phi=0$ and $2s^p$ meaning $n_\xi=0$, $n_\eta=1$, $n_\phi=0$, or, the meanings of $2s^s$ and $2s^p$ might be interchanged; in either case $2p^p$ surely means $n_\xi=0$, $n_\eta=0$, $n_\phi=\pm1$. In any case, the energy order is very different than for spherical coordinates. That no uniform correspondence of n_r to n_ξ and n_θ to n_η, or vice versa, can be expected appears to follow from Hund's work, although in particular cases a definite correspondence may perhaps be predictable. So far as the theory goes at present, it appears that we may be prepared to find either or both correlations in practice, even with the possibility of opposite correlations for different electrons in the same molecule.

Results similar to those of Table V can readily be given for any desired configuration of electrons. (Results are always independent of any closed shells which may be present.) The results depend on $\sigma_{l\tau}$, not on n_τ and l_τ, e.g. two $4p^d$ or two $4p^f$ electrons give the same molecular states ^3S, ^1S, and ^1D as two $2p^p$ electrons. Two *different* electrons (e.g. $4p^d$ and $4p^f$) of course give additional possibilities (here ^3D), since the Pauli restrictions are dropped. *One* np^x ($x=p$, d, f, etc.) electron obviously gives a *normal* ^2P state only. *Three* np^p or np^x electrons probably give only an *inverted* ^2P; the reasons are given in the following paragraphs; addition of an s^x electron to such as an inverted ^2P state should yield a ^1P and an inverted ^3P state. From the results given up to this point, together with others obtained by the same methods, everything given in Table I of the text can be readily obtained.

Proof of inverted character of ^2P *from* (X) $(np^x)^3$. As Slater has pointed out,[69] the energy differences in the multiple electron levels in atoms are caused mainly by the interaction of the l of each electron with *its own* s. If there are several electrons, the interaction energy is of the form $\Sigma_\tau A_\tau l_\tau \cdot s_\tau$, l_τ and s_τ here representing the l and s *vectors* of the τ'th electron.[70] When all the electrons are equivalent, we may put $A_\tau=A$ for all. For a molecule with the type of quantum numbers here used, each term $A_\tau\, l_\tau \cdot s_\tau$ reduces

[69] J. C. Slater, Phys. Rev., **28**, 291 (1926). Cf. also ref. 15, p. 121 *et seq.*

(noting that $s=\frac{1}{2}$) to $\frac{1}{2}A_\tau\ \sigma_{l\tau}\cos(\sigma_{l\tau}, s_\tau)$[70]. For the case of *one* p electron in a molecule, the energy is then $A/2$ for $^2P_{1\frac{1}{2}}$ and $-A/2$ for $^2P_{\frac{1}{2}}$. For the case of *three equivalent* p electrons ($\sigma_{l\tau}=1$ for each) it will be seen by referring to Fig. 1, and performing the summation $\frac{1}{2}A\Sigma_\tau\cos(\sigma_{l\tau}, s_\tau)$, that the

Fig. 1.

energy is $-A/2$ for $^2P_{1\frac{1}{2}}$ and $+A/2$ for $^2P_{\frac{1}{2}}$. Fig. 1 involves the assumption that the coupling of the spins of equivalent electrons is such that the individual spins are either parallel or anti parallel to their resultant, s; since the electric field should not affect the spin coupling (cf. above), this assumption, which is valid for atoms, should be equally true for molecules.[70]

It is desirable to show that these results are independent of the assumed choice of quantum numbers. If the tendency is toward elliptical quantum numbers, $\sigma_{l\tau}$ still corresponds to the average angular momentum, and nothing is changed. If the tendency is toward a coupling of l_τ's to a resultant l, the individual $\sigma_{l\tau}$'s are lost; we can determine how things are going by proceeding to the limiting case of the united atom. Here there are several possibilities, since any ns^p electrons which may be present must be considered as well as the np^p electrons. The two extreme possibilities are as follows: (1) The molecular configurations $(X)\ (ns^p)^2(np^p)^3$, ^2P and $(X)\ (ns^p)(np^p)^4$, ^2S, taken together, go over into a ^2P state of a united atom of the halogen type with, in the atomic sense, *five* equivalent p electrons; such a ^2P atomic state is always inverted.[15] (2) From an $(X)\ (np^p)^3$, ^2P molecular state without ns^p electrons, taken together with some appropriate ^2S state of the $(X)\ (ns^p)\ (np^p)^2$ type, we get a ^2P united-atom state of the same kind as in an atom with *three* equivalent p electrons, i.e. a state like the predicted low-lying metastable ^2P state of the N or O^+ atom; for such a state the doublet separation is approximately zero.[71]. Since this second limiting case will not be closely approached in the molecule, we may reasonably expect an inverted ^2P in all cases for a molecule with three equivalent np^x electrons.

In Part II of this paper, in a subsequent issue, the evidence for the "Probable Products of Dissociation" listed in Table III will be discussed, and various conclusions, arising from these and other results summarized

[70] A revised interpretation of the cosines in Slater's formula is required according to the quantum mechanics (cf. S. Goudsmit, Phys. Rev., **31**, 946, (1928), but it seems fairly clear that these changes will not affect the qualitative conclusions stated in the text, especially since the changes required for cos $(\sigma_{l\tau}, s_\tau)$ are probably less than for cos (l_τ, s_τ).

[71] Cf. Bowen's data on the s^2p^3 (aP) state of O_{II} and of F_{III}: Phys. Rev., **29**, 243 (1927).

in Table III, will be brought out in Part II and later papers. These conclusions have to do with the changes which atomic electrons undergo in the formation of a molecule, and also bear on the problems of valence and chemical stabilities. In later papers other molecules will also be considered.

WASHINGTON SQUARE COLLEGE,
NEW YORK UNIVERSITY,
April 30, 1928.

THE ROTATIONAL STRUCTURE OF THE BLUE-GREEN BANDS OF Na_2

By F. W. Loomis[1] and R. W. Wood[2]

Abstract

Because of the theoretically impossible structure of these bands as reported by previous observers, the writers have measured them, in absorption, in the third order spectrum of a seven inch plane grating mounted in a forty foot spectrograph. Each band is found, quite definitely, to consist of only one P, one Q and one R branch. This accords with Mulliken's theory that the electronic transition is $^1P - ^1S$, and with the nature of the fluorescence series. Moreover the absorption series correlate properly with the fluorescence series. The combination relations have been applied to all measured bands and found to hold, rigorously, within the experimental error, except for the expected PQR defect, which is very small.

Constants of the band system.—The more important constants of this band system are: $B_0'' = 0.15431$, $I_0'' = 179.5 \times 10^{-40}$ g. cm^2, $r_0'' = 3.08 \times 10^{-8}$ cm, $\alpha'' = 0.00082$, $B_0' = 0.12541$, $I_0' = 220.9 \times 10^{-40}$ g. cm^2, $r_0' = 3.41 \times 10^{-8}$ cm, $\alpha' = 0.00094$. These extremely large internuclear distances correspond to weak molecular binding, which is in accord with the low heat of dissociation previously reported. The locus of most intense vibrational transitions calculated from these constants and the previously reported vibrational constants, by the method of Franck and Condon, is found to be a good representation of the observed distribution. There is no evidence of alternating intensities.

THE visible band absorption spectrum of Na_2 consists of two distinct band systems, one in the red, the other in the blue-green. Each contains numerous overlapping bands and each band contains hundreds of lines, so that the spectrum is extraordinarily complicated. In complexity and line density it is about on a par with the spectrum of iodine.

The vibrational structure of the blue-green system has been analyzed and vibrational quantum numbers assigned by Loomis,[3,4] from a study of Wood's magnetic rotation spectrum.[5,6] The same assignment of vibrational quantum numbers has been reached by Fredrickson and Watson,[7] using their measurement of the frequencies of the heads in absorption, and is undoubtedly correct.

Rotational structure lines of what are now known to be the (1,1), (2,0), (3,0) and (5,1) bands were measured in absorption by Smith,[8] with a grating which gave a dispersion of 5A/mm and was able to resolve lines about 0.1A apart. He also arranged his lines into series, assigned quantum num-

[1] New York University.
[2] The Johns Hopkins University.
[3] Loomis, Phys. Rev. **29**, 607A (1927).
[4] Loomis, Phys. Rev. **31**, 323–332 (1928).
[5] Wood, Proc. Am. Acad. **42**, 235 (1906).
[6] Wood, Astrophys. J. **30**, 339 (1909).
[7] Fredrickson and Watson, Phys. Rev. **30**, 429–437 (1927).
[8] Smith, Proc. Roy. Soc. **A106**, 400–415 (1924).

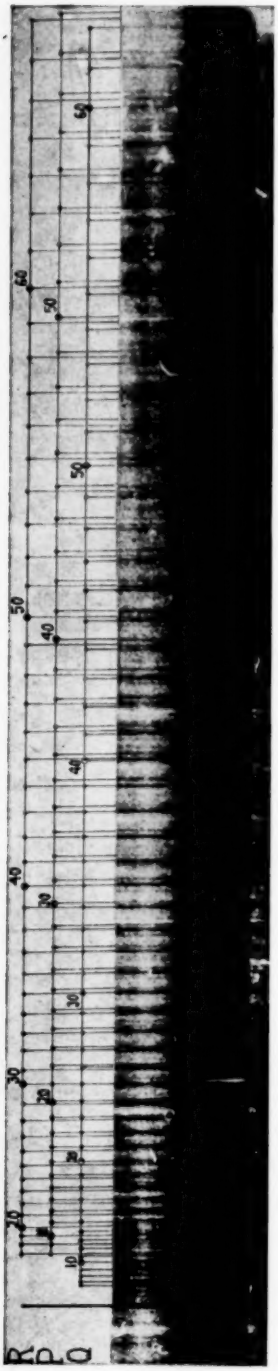


Fig. 1. (0, 2) band. Numbers indicate values of j''.

bers to them, and calculated the moments of inertia of the molecule. He did not, however, check his assignments by the combination relations; and in fact when the PR combinations are tested on his data they fail completely. Moreover, the (1,1) band, as reported by him contains four branches, (R, Q, P, P') which, according to Mulliken's[9,10] system of interpretation of band spectra, is not a possible structure for molecules having an even number of electrons.

More recently the structure lines of the (1,0), (1,1), (0,1) and (0,2) bands have been measured by Fredrickson and Watson,[7] in the second order of a 21 ft. concave grating, giving a dispersion of 1.3/Amm. They arrange the lines of each band into four series which they call R, Q_R, Q_P and P, and which are quite different from those of Smith. They did apply the combination relations to check their arrangement into series and their assignment of quantum numbers, but their PR combinations show a systematic defect, and fluctuations of the order of magnitude of the line spacing. Moreover, the four branch structure which they report does not correspond to any of the types to be expected according to Mulliken's systematic theory of band spectra; certainly not to the $^1P-{}^1S$ transition which is indicated by the character of the fluorescence series.[11]

The writers therefore felt that it was desirable to undertake new measurements of these bands, with higher resolution than previous observers have used, in the hope of finding series whose reality could be unambiguously established and of definitely determining whether or not these bands constitute an exception to Mulliken's system.

The spectrum was photographed in the third order of a 7 inch (17.8 cm) plane grating ruled with 14,000 lines per inch and combined in a Littrow mount with a 40-foot telescope lens as previously described by Wood.[12] This

[9] Mulliken, Phys. Rev. **28**, 481 (1926).
[10] Mulliken, Phys. Rev. **28**, 1202–1222 (1926).
[11] l.c. page 1216.
[12] Wood, Researches in Physical Optics, I, 27–29.

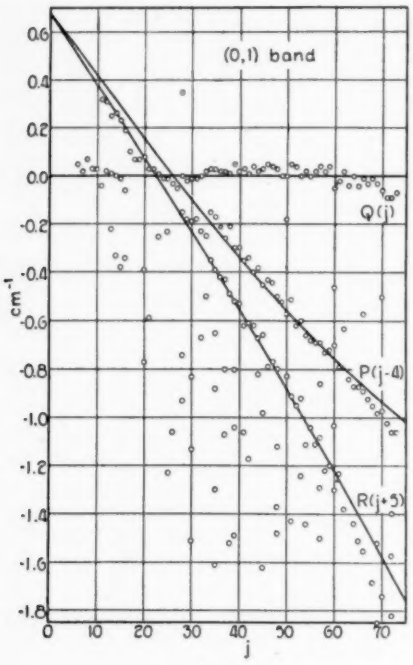
gave a dispersion of 0.4A/mm and resolved lines as close as 0.03A. The sodium was inserted in a steel tube about 80 cm long, to the ends of which glass windows were cemented. The tube was heated in a gas flame and the hydrogen thereby driven from the sodium was pumped off until a fairly steady pressure of a few mm was attained. The light from the crater of a carbon arc was then sent through the sodium vapor and into the slit of the spectroscope. The heating flame was carefully regulated to give just sufficient density of Na_2 to bring out the stronger lines fairly well, leaving the fainter lines inconspicuous. This condition was reached when the transmitted light was of a pale-green color and the corresponding absorption spectrum was relatively simple. If the temperature of the sodium was raised until the color of the transmitted light was deep blue, ahe absorption spectrum became very complicated and would probably have defied analysis. The absorption spectrum was photographed, with the iron arc lines for comparison, from 4890 to 5035A, as this region contains the origin of the system and the strong (0,1), (0.2), (1,0) and (1,1) bands which Fredrickson and Watson measured. It also contains a number of fainter bands.

A photograph of the (0,2) band, in which there is a minimum of overlapping lines, is reproduced in Fig. 1. It is evident that it consists of just three branches, as predicted by Mulliken's theory. The identification of the lines, as found from the analysis below, is indicated above them.

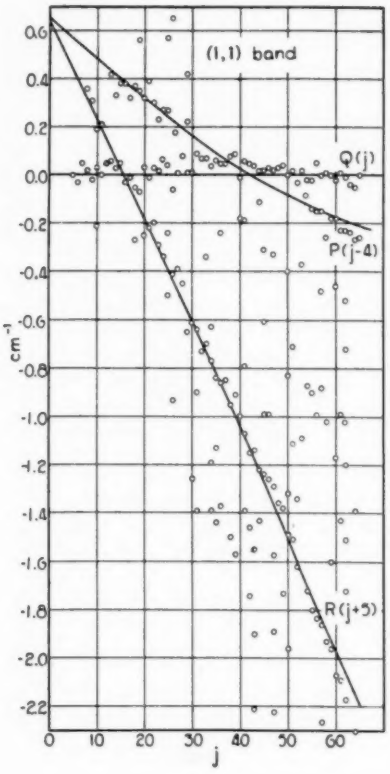
The other bands in the region studied are so complicated by overlapping lines that the series cannot be followed by inspection. They can, however, be followed in a table of computed line frequencies with estimated intensities, and it is quite evident that there are just three branches starting from near the head of each band. This will be apparent to the reader on inspection of Fig. 2. In this figure are plotted the differences between the frequency of every line in the *region* of the (0,1), (0,2), (1,0) and (1,1) bands, and the frequency of the adjacent Q branch line as calculated from Eq. (16) below. This method of plotting shows any series of lines which have roughly the same spacing as the Q branch, that is, any other branches of the same band, as a series of points lying along a smooth curve; whereas the lines of overlapping bands are represented by points scattered at random over the figure. The reality of the three series which appear in each band is even more evident when the intensities are noted, since in most cases the scattered points represent lines of lower intensity than those assigned to branches. It is then also apparent that the Q branch lines are, as predicted by Mulliken's theory,[13] definitely more intense than the R or P lines. In fact, in the (0,0) band, which is comparatively faint and overlapped by stronger bands, the Q branch is the only one which could be clearly demonstrated by this method.

It was next necessary to decide which series were P, which Q and which R branches and to determine which lines in each series had the same j''. Unfortunately the frequencies of the lines in Wood's fluorescence series are not quite accurately enough known to be used for this purpose; but

[13] Mulliken, Phys. Rev. **29**, 391–412 (1927).



2a



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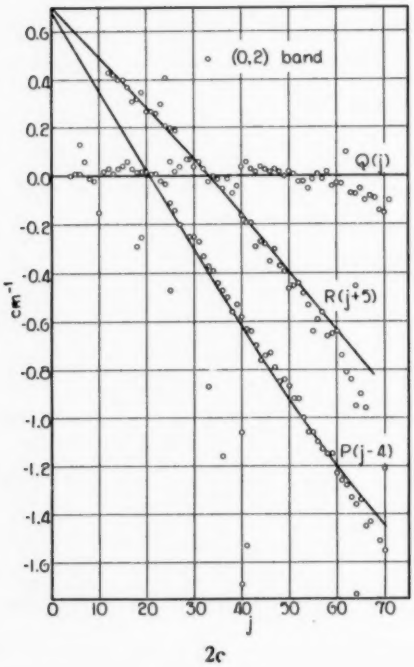

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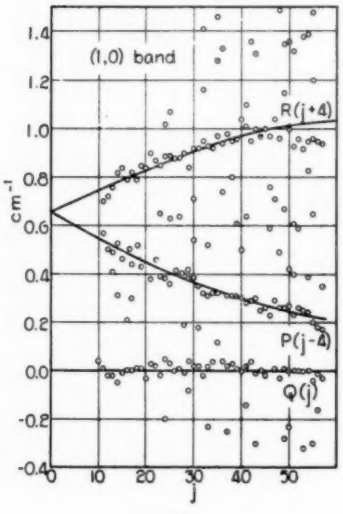


2d

Fig. 2. $\nu - Q(j)$ for lines in the region of the four measured bands. $Q(j)$ from Eq. (16) and Table I. The curves show the positions of the P, Q and R lines calculated from Eqs. (16) and (17).

the accuracy of the measured frequencies of the absorption lines is great enough to allow the determination to be made by the aid of the combination relations. This was done by a process of trial and error, using the fluorescence data to make tentative pairings of lines in the P and R branches. The final correct assignment of relative values of j'' to the P and R branch lines was attested by the agreement, within the limit of experimental error, of the values of

$$\Delta_2F''(j)=R(j-1)-P(j+1) \quad (1)$$

for bands (0,1) and (1,1)

and $\Delta_2F'(j)=R(j)-P(j)$ for bands (0,1) and (0,2) and for bands (1,0) and (1,1). In each case the next best assignment led to discrepancies between the Δ_2F's which were definitely outside the experimental error over some part of the range. The exactness with which these PR combination relations hold may be seen in Fig. 3, wherein the residuals of the Δ_2F's from functions obtained below, which represent them, are plotted against the j values, also obtained below. It is true that there are a few places in which there appear to be slight systematic differences between the Δ_2F's, over a series of several values of j, but these occur where the lines of two branches of a band are unresolved; as may be seen by comparing with Fig. 2. In no case does the discrepancy become as large as the resolution of the grating.

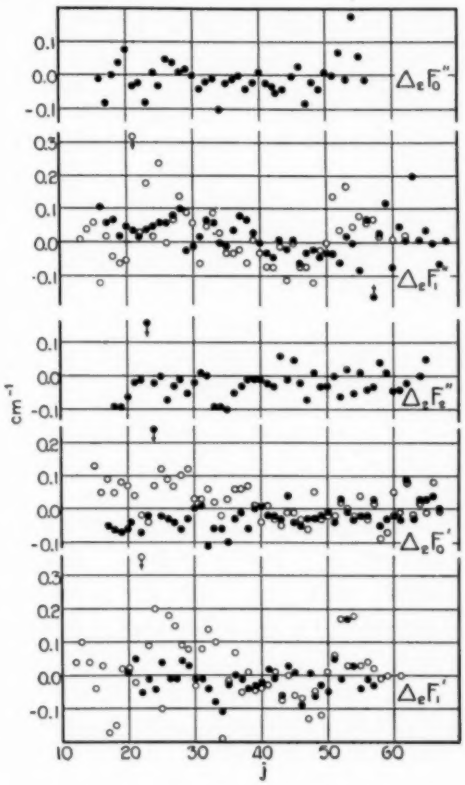


Fig. 3. Δ_2F, (observed)–(calculated by Eqs. (13) and (15)). Reading down, full circles represent data from bands (1, 0), (0, 1), (0, 2) (0, 2) and (1, 0); hollow circles represent data from bands (1, 1) (0, 1) and (1, 1).

It is not to be expected that the PQR combinations would hold exactly. This may be seen from Fig. 4, which illustrates the scheme of energy levels associated, according to Mulliken,[14] with a $^1P-{}^1S$ transition. Rotational doubling of the ^1P levels is to be expected. That is, there should be two terms, F_Q and F_{PR}, for each value of j, the F_Q terms taking part only in Q transitions, the F_{PR} terms only in P and R transitions. From an inspection of the diagram it can be seen that the "quantum defect"

$$[R(j)-Q(j+1)]-[Q(j)-P(j+1)]$$
$$=[F_{PR}'(j+1)-F_Q'(j+1)]+[F_{PR}'(j)-F_Q'(j)] \quad (2)$$

[14] Mulliken, Phys. Rev. **28**, 1205 (1926). The relative position of the PR and Q levels is here interchanged from that in Mulliken's figure, since this is how they happen to lie in Na_2, as is shown by the sign of the combination defect.

$$\sim 2[F_{PR}'(j+\tfrac{1}{2})-F_Q'(j+\tfrac{1}{2})]=2(B_{PR}'-B_Q')(j+\tfrac{1}{2})^2 \qquad (3)$$

This quantity is plotted, for each of the four bands, in Fig. 5. The curve drawn through them is calculated according to (3) using $B_{PR}-B_Q=0.000013$, determined by least squares.

On account of the theoretically possible quantum defect, the above relations do not furnish an unquestionable check on the Q branches, though

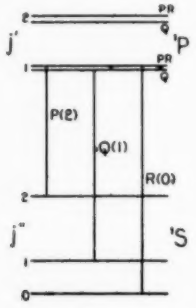


Fig. 4. Rotational energy levels and transitions associated with a $^1P-{}^1S$ electronic transition.

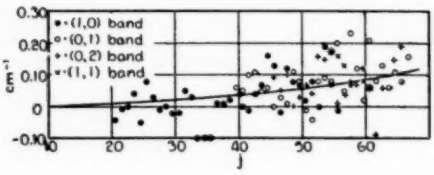


Fig. 5. PQR quantum defect.

the quantum defect is so very much less for this assignment of numbers than for any other, and so closely the same for all four bands, that there cannot be much real doubt. To make doubly sure however, the four band combinations have been applied to the Q branches. For this purpose data

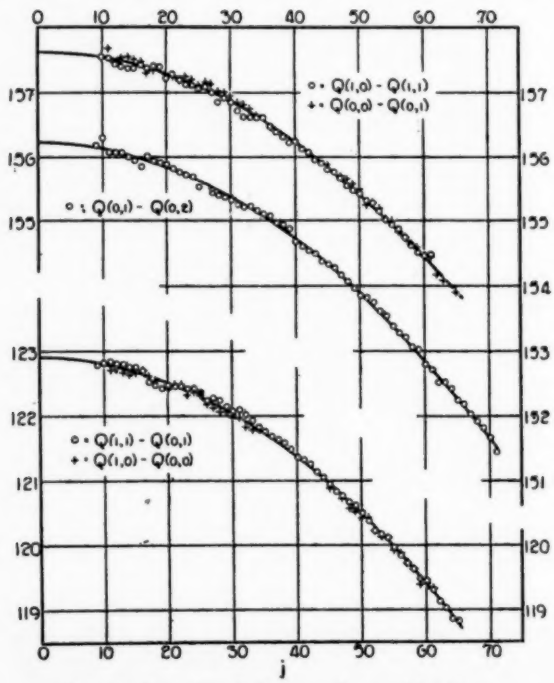


Fig. 6. Four-band Q branch combinations.

on the Q branch of the (0,0) band were also needed. Fig. 6 shows the result, which is quite conclusive. In the upper curve $Q(1,0)-Q(1,1)$ and $Q(0,0)-Q(0,1)$ are plotted and found to agree except where one of the four branches is overlapped by another. In the lowest curve, $Q(1,1)-Q(0,1)$ and $Q(1,0)-Q(0,0)$ are plotted and likewise agree.

When the above frequency differences had been obtained, the constants of the spectrum were computed by the following procedure. Absolute values of j were found by plotting the frequency differences $\Delta_2 F$, Eq. (1), against an assumed set of j's and extrapolating to zero. In each case, if the new mechanics formulation of the rotational term, $B[j(j+1)-\sigma^2]$ or its practical equivalent $Bj(j+1)$, is used, the values of j are found to be integral within the limits of error. They were therefore assumed in all subsequent calculations to be exactly integral and this assumption was later justified when more accurate least-squares computations were made after the $\Delta_2 F$'s had been corrected for the higher power terms in the energy. Approximate values of B' and B'' were found at the same time. Values of $B_0'-B_1'$, $B_0''-B_1''$ and $B_1''-B_2''$ and of $\Delta\nu_0$ were then found which were capable of representing the differences:

$$\begin{aligned}
Q_{1,1}(j)-Q_{0,1}(j) &= Q_{1,0}(j)-Q_{0,0}(j) \\
&= \Delta\nu_0-(B_0'-B_1')j(j+1)=122.92-0.00094j(j+1) \\
Q_{1,0}(j)-Q_{1,1}(j) &= Q_{0,0}(j)-Q_{0,1}(j) \\
&= \Delta\nu_0-(B_0''-B_1'')j(j+1)=157.64-0.00085j(j+1) \\
Q_{0,1}(j)-Q_{0,2}(j) &= \Delta\nu_0-(B_1''-B_2'')j(j+1)=156.23-0.00091j(j+1)
\end{aligned} \tag{5}$$

as follows:

$$B_0'-B_1'=0.00094,\ B_0''-B_1''=0.00085,\ B_1''-B_2''=0.00091, \tag{6}$$

an approximate preliminary computation having first corrected for the effect of the nearly negligible higher power terms. The curves in Fig. 6 represent the frequency differences calculated from these constants.

A change of 0.00001 in any of the B differences above would just about make a sensible deviation of the curve from the plotted points, so the B differences may be assumed to be correct to about 0.00001. The difference between $B_0''-B_1''$ and $B_1''-B_2''$ is therefore real, and a linear formula is insufficient to represent the values of B''. The quadratic formula which does represent them is

$$B''(n'')=B_0''-\alpha''n''-\alpha_2''n''^2=B''-0.00082n''-0.00003n''^2. \tag{7}$$

Since only one difference, $B_0'-B_1'$ is available in the upper level, the best that can be done is to assume that it is equal to α'.

$$B'(n')=B_0'-\alpha'n'=B_0'-0.00094n' \tag{8}$$

The coefficients of the higher powers of j in the rotational terms could then be calculated. It was only necessary to carry the expansion as far as j^4, i.e.

$$F_n(j) = B_n[j(j+1)-\sigma^2]+D_n[j(j+1)-\sigma^2]^2 \tag{9}$$

In this expansion σ makes no practical difference. Here D_0' and D_0'' can be calculated from Kratzer's[15] formula $D_0 = -4B_0^3/\omega_0^2$ and the other values of D can be found from $D_n = D+\beta''n$ after $(\beta'')'$ and $(\beta'')''$ have been computed from Pomeroy's[16] version of Kemble's[17] formula. For this purpose values of ω_0 and x were taken from Loomis' formula,[4]

$$\nu = 20301.7+(124.13n'-0.84n'^2)-(158.5n''-0.73n''^2-0.0027n''^3) \tag{12}$$

for the vibrational levels of the green system.

Corresponding to Eq. (9) for $F(j)$, the expression for the $\Delta_2F(j)$ of Eq. (1) is

$$\Delta_2F(j) = 4B(j+\tfrac{1}{2})+8D(j+\tfrac{1}{2})^3 \tag{13}$$

except for some negligible terms. The previously tabulated values of Δ_2F can now be corrected by the addition of $-8D(j+\frac{1}{2})^3$ to give

$$\Delta_2F^*(j) = 4B(j+\tfrac{1}{2}) \tag{14}$$

which should be strictly proportioned to $j+\frac{1}{2}$. From the tables of values of Δ_2F^*, B's were calculated according to Eq. (14) by least squares after it had first been ascertained by least squares that, with the values of j which had previously been assigned, there was actually no additional constant term in (14) larger than the limit of error of the determination; that is, that the j's were actually the integers which had been assumed. These values of B were than slightly adjusted, by no more than 1 in the last figure, to make them agree with Eqs. (6). The final values of B and D are as follows:

$$\left.\begin{aligned} B_0' &= 0.12541 \\ B_1' &= 0.12447 \end{aligned}\right\} \text{ for } P \text{ and } R \qquad \left.\begin{aligned} B_0'' &= 0.15431 \\ B_1'' &= 0.15346 \\ B_2'' &= 0.15255 \end{aligned}\right.$$

$$\left.\begin{aligned} B_0' &= 0.12540 \\ B_1' &= 0.12446 \end{aligned}\right\} \text{ for } Q \text{ branches} \qquad \left.\begin{aligned} D_0'' &= -0.5860\times10^{-6} \\ D_1'' &= -0.5907\times10^{-6} \\ D_2'' &= -0.5954\times10^{-6} \end{aligned}\right. \tag{15}$$

$$\left.\begin{aligned} D_0' &= -4.076\times10^{-6} \\ D_1' &= -4.127\times10^{-6} \end{aligned}\right.$$

Fig. 3 represents the residuals of the observed values of Δ_2F from those calculated according to Eq. (13) with the constants in Eqs. (15). This figure shows at the same time the exactness with which the combination relations hold and the exactness with which the constants in (15) represent the observed values of Δ_2F.

The remaining unknown constant, the origin of the system, was found from the frequencies of each of a number of representative lines. The accepted average is ν_0 (0,0) = 20301.70.

[15] Kratzer, Zeits. f. Physik. **3,** 289 (1920).
[16] Pomeroy, Phys. Rev. **29,** 69 (1927).
[17] Kemble, J.O.S.A. **12,** 1 (1926).

The frequencies of the lines of the bands can now be calculated from the above constants according to the following equations;

$$Q(j)=\nu_0+C_Q(j+\tfrac{1}{2})^2+E(j+\tfrac{1}{2})^4 \tag{16}$$

$$R(j) \text{ or } P(j)=\nu_0+B'\pm 2B'_{PR}(j+\tfrac{1}{2})+C_{PR}(j+\tfrac{1}{2})^2\pm 4D'(j+\tfrac{1}{2})^3+E(j+\tfrac{1}{2})^4 \tag{17}$$

$$\text{where} \quad C_Q=B_Q'-B'', \; C_{PR}=B_{PR}'-B'' \text{ and } E=D'-D''. \tag{18}$$

These are equivalent to the expressions deducible from Eq. (9) if a few negligible terms are omitted. The constants ν_0, C and E of the five bands measured are given in Table I.

TABLE I. *Values of the constants for the five bands measured.*

Band	ν_0	C_{PR}	C_Q	E
0, 0	20301.70	−0.02890	−0.02891	7.65×10^{-8}
0, 1	20144.06	−0.02805	−0.02806	8.12×10^{-8}
0, 2	19987.83	−0.02714	−0.02715	8.59×10^{-8}
1, 0	20424.64	−0.02984	−0.02985	7.02×10^{-8}
1, 1	20267.00	−0.02899	−0.02900	7.49×10^{-8}

Fig. 7 is a Fortrat diagram of the (0,2) band in which the observed frequencies are indicated by the circles and the calculated ones by the curves. On this scale the agreement appears to be perfect.

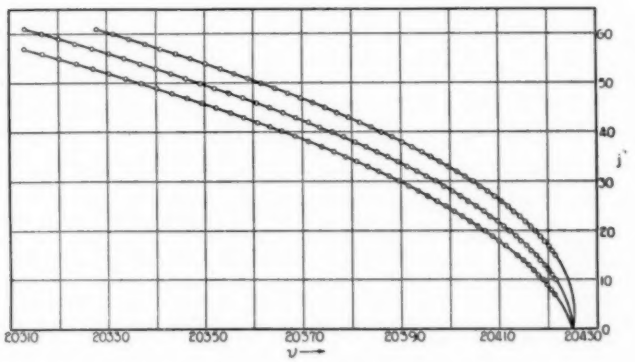


Fig. 7. Fortrat diagram of (0, 2) band.

In Fig. 2 the calculated differences between the lines of the several branches and the adjacent Q branch lines are represented by the curves. On this large scale it is apparent that there are slight but real systematic differences between the calculated and observed frequencies. However, they correspond to errors of only about 1 in the last figure of C and of 3 or 4 in the second figure of E, which are within the probable error of the determination of these constants from the $\Delta\nu$'s. It is not to be expected that constants determined from the $\Delta\nu$'s can be accurate enough to represent the ν's themselves adequately. The B's and D's could be adjusted within the probable error, to yield C's and E's which would accurately represent the ν's, but this procedure is not worth while, since it would not result in any gain in

accuracy in the B's. This is because each $C=B'-B''$ and there is no way to tell how to divide the adjustment between B' and B''.

The accurate values of B_0' and B_0'' in Eqs. (15) can now be used to calculate the moments of inertia and internuclear distances of the molecule according to the equations:

$$B_0 I_0 = h/8\pi^2 c = 27.70\times 10^{-40} \tag{19}$$

$$I_0 = \tfrac{1}{2} m r_0^2 \tag{20}$$

Here m is the mass of a sodium atom, 3.80×10^{-23} grams. The resulting values of the molecular constants are:

$$I_0'' = 179.5\times 10^{-40}\ \text{g.cm}^2, \qquad r_0'' = 3.08\times 10^{-8}\ \text{cm},$$

$$I_0' = 220.9\times 10^{-40}\ \text{g.cm}^2, \qquad r_0' = 3.41\times 10^{-8}\ \text{cm}.$$

These are extremely large internuclear distances, indicative of a loosely bound molecule. They are therefore in qualitative accord with the small heats of dissociation, 1.0 volt in the lower and 0.6 volt in the upper state, already reported by Loomis.[4]

The present analysis of the structure of these bands is in harmony with the evidence of the fluorescence series. It is obvious that, if Fig. 4 is the correct energy level diagram, and the establishment of the PQR defect indicates that it is, then a fluorescence series should consist of doublets or singlets, according as the excited molecule happens to be in a PR or a Q state. All of Wood's data[5,6] on the fluorescence spectra of sodium excited by various line sources have been examined for the existence of series by a method like the one used by Loomis[18] to find iodine fluorescence series. That is, when, as is usually the case, the fluorescence lines fall naturally into groups separated by approximately ω'', these groups are assigned an "order" number p, starting with the group which contains the exciting line. (In some cases where there are many anti-Stokes lines it is more convenient to assign a "pseudo-order," p^*, starting with the lowest anti-Stokes group.) $\nu+T''(p)$ for each line is then plotted against p. In this arrangement singlet fluorescence series are represented by straight lines and doublet series by pairs of approximately parallel straight lines. The slope of the lines enables one to identify the bands to which the various members of the series belong. It was found that, while many of the fluorescence spectra are too complicated, resulting from simultaneous stimulation by too many lines, and often are too inaccurately measured, to permit unambiguous determination of series, there are many spectra in which definite singlet series exist, and a few in which there are definite doublet series, but none in which there is a triplet series. This is as it should be.

Moreover two of the doublet series, those excited by the 5086A line of Cd and the 5006A line of Pb, and a singlet series excited by Li 4972 have members which lie in the region where we have measured the absorption lines. These provide a further check on our work, since all members of a

[18] Loomis, Phys. Rev. **29**, 112–134 (1927).

doublet series must correspond to P and R absorption lines having the same j' and n', and all members of a singlet series to Q lines having the same j' and n'. In Fig. 8 the fluorescence lines excited by Pb 5006A are represented

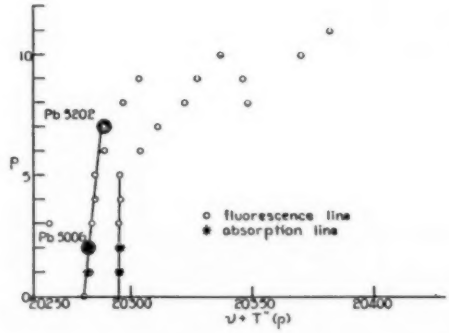
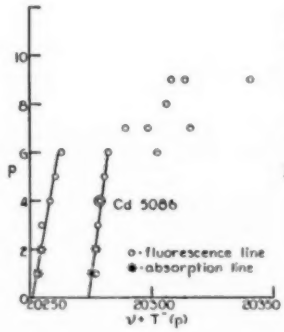


Fig. 8. Doublet fluorescence series excited by Pb 5006. P and R absorption lines with $n'=0$ and $j'=21$.

by circles, using the coordinates described above, while the P and R absorption lines with $j'=21$ from the (0,1) and (0,2) bands are represented by crosses. In Fig 9 the fluorescence lines excited by Cd 5086A are represented by circles and the P and R absorption lines with $j'=36$ from the



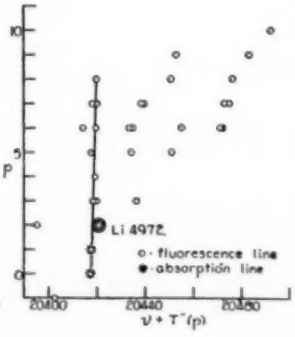


Fig. 9. Fig. 10.

Fig. 9. Doublet fluorescence series excited by Cd 5086. P and R absorption lines with $n'=0$ and $j'=36$.

Fig. 10. Singlet fluorescence series excited by Li 4972. Q absorption lines with $n'=1$ and $j'=15$.

same two bands are represented by crosses. In Fig. 10 the fluorescence lines excited by Li 4972 are represented by circles and the Q absorption lines with $j'=15$ from the (1,0) and (1,1) bands are indicated by crosses. It will be seen that the fluorescence and absorption frequencies agree within the apparent error of the measurements of the fluorescence spectra, and that the absorption frequencies lie more closely on the lines representing fluorescence series. Our absorption measurements are then very satisfactorily checked by the fluorescence series.

Two semi-empirical rules recently enunciated by Mecke and Birge and found to hold remarkably well in many varied spectra, furnish additional checks on the correctness of our analysis of these bands. The first rule is that B_0/ω_0 remains approximately constant during a transition.[19] Our values of the constants yield $B_0''/\omega_0''=0.00097$, $B_0'/\omega_0'=0.00101$. The second rule[20] is that the quantity $R=2xB_0/\alpha$ must be greater than 1, is usually between 1.2 and 2.2 and is roughly constant during a transition. Our constants yield $R''=1.73$, $R'=1.81$.

The constants B_0'', B_0', α'' and α' obtained from the above analysis, together with ω_0'', ω_0', x'', x', D'' and D' from Loomis' analysis[4] of the vibrational structure, furnish sufficient data for a good determination of the locus of most intense vibrational transitions according to the method of Franck[21] and Condon.[22] Fig. 11 shows the potential energy in the lower

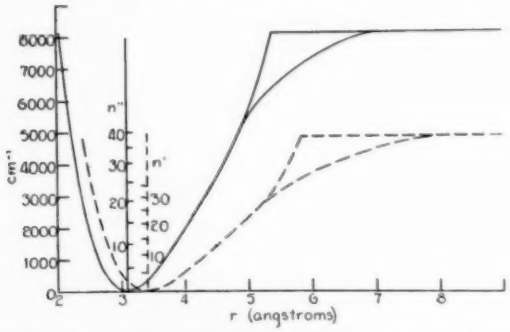


Fig. 11. Potential energy of Na_2 molecule as a function of internuclear distance. The lower state is represented by a continuous line, the upper state by a broken line.

state (continuous curve) and in the upper state (broken curve) as a function of internuclear distance r. The lower parts of these curves represent Taylor's series expansions about the equilibrium positions with coefficients calculated according to Condon's equations. The horizontal asymptotes represent the energies of dissociation. Smooth transitions between the two have been drawn in arbitrarily.

The curve in Fig. 12 is the (n', n'') locus of most probable vibrational transitions, obtained from Fig. 11 by Condon's procedure. The numbers in the circles represent the intensities of the magnetic rotation lines, plotted at the values of (n', n'') to which they were assigned by Loomis.[4] Although the curve deviates somewhat from the observed bands of high n'', as do most such curves, the agreement is on the whole excellent. The same curve represents equally well the absorption head measurements of Fredrickson and Watson.[7]

We have been to some pains to subject our analysis to all possible proofs because it is completely different from both those previously pub-

[19] National Research Council Report on "Molecular Spectra in Gases," page 233.

[20] Birge, private communication.

[21] Franck, Trans. Faraday Society (1925).

[22] Condon, Phys. Rev. **28,** 1182–1201 (1926).

lished. Thus Smith's values of B are about 8 times and Fredrickson and Watson's from 2 to $2\frac{1}{2}$ times as great as ours; and the lines of Smith's series and of Fredrickson and Watson's series are spaced at more than double the intervals of ours. According to our analysis, lines of their "series" belong successively to a P branch, a Q branch, an unresolved chance pair of lines, etc. That is, their series are completely illusory, probably because of the lack of sufficient resolution. Since Fredrickson and Watson also considered the combination relations and the same fluorescence lines as evidence for the reality of their series it is necessary to give here a comparative summary of the evidence.

The following are evidence in favor of the reality of our series and the correctness of our analysis; (a) the type of band structure agrees with the existence of singlet and doublet fluorescence series and with Mulliken's

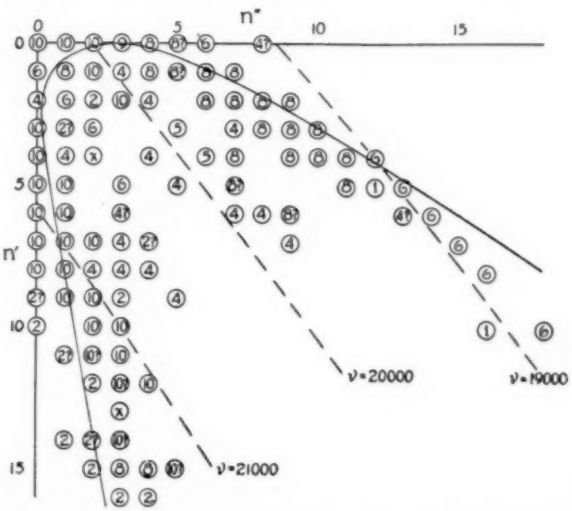


Fig. 12. Calculated locus of most probable vibrational transitions. Numbers in circles represent intensities of corresponding magnetic rotation lines.

theory; (b) three series are evident in each band in Fig. 2; (c) each series of fluorescence lines corresponds to absorption lines with a single j'; (d) and (e) the PR combination relations and the four band Q combination relations hold within the limits of error of measurement; (f) the PQR combinations show the same very small defect for each of the four bands, (g) the $\Delta_2 F$'s show a deviation from linearity for high values of j, and this deviation agrees with the theoretically calculated cubic term; (h) B_0/ω_0 and $R=2\times B_0/\alpha$ behave as predicted according to Birge and Mecke's semi-empirical relations; (i) when our constants are used to calculate the locus of (n', n'') for bands of maximum intensity, according to the Franck-Condon method, the curve obtained is a good representation of the observed distribution.

None of the above checks was applied by Smith to his series, and of those which can be applied, (a), (d) and (f) definitely disprove them. When applied to Fredrickson and Watson's series, (c) holds as well as it does for

ours; insufficient data are available for the application of (b), (e) and (g); the combinations (d) show systematic trends appreciably larger than the probable error, and large fluctuations; the combination defect in (f) is of the order of magnitude of $\Delta\nu$ itself; and (a), (h) and (i) definitely fail. In particular, the values of R calculated from Fredrickson and Watson's constants are $R''=0.32$ and $R'=0.18$ whereas, according to Birge's theory, R must always be greater than unity.

It should be mentioned that there is no evidence of any alternation of intensities in the absorption lines of these bands. Of course the intensities were estimated only visually, and any determination of intensities in absorption is notoriously rough, and there is here the complication of overlapping bands. Nevertheless the spectra show quite definitely greater intensities of the Q branch lines over the R and P lines, which should, on Mulliken's theory[13] be about half as intense. In many cases, near the tails of the bands, the R lines are perceptibly less intense, as they should be, than the adjacent P lines, but still show no trace of alternating intensities. It is probably safe to say that there is no alternation of intensities with a ratio between adjacent lines of over 3/2 or even 4/3.

THE ALFRED LOOMIS LABORATORY
TUXEDO PARK, N. Y.
April, 1928.

AN APPROXIMATION METHOD AND APPLICATION TO SOME HCl BANDS

By D. G. Bourgin

Abstract

A method of approximation applicable to some experimental investigations is based on the inversion for $\mu(\nu)$ of the integral equation

$$A(x)=\int_0^\infty (1-e^{-\mu(\nu)x})d\nu$$

The general nature of the interdependence of $A(x)$ and $\mu(\nu)$ is described and a practicable method of characterizing certain types of $\mu(\nu)$ is developed in sufficient detail to permit of immediate application of the results. The author's previously published data for the HCl fundamental band lines has been approximated by line patterns based on the hypothesis of (a) a Doppler broadening or error curve structure, (b) a Stark broadening due to the molecular force field set up by neighboring molecules, and (c) an interrupted absorption process or dispersion curve type. The modifications attendant on recognizing the isotopic doubling of the lines are predictable from the calculation for a doublet structure of infinite component separation. The values of the line intensities and breadths and the Einstein coefficients A_{01} and B_{01} are given for each of the assumed structures. Kinetic theory considerations make it improbable that the Doppler effect is the primary determining influence as regards line shape. The Lorentz line with a possible Doppler broadening superposed would seem to reproduce the experimental data satisfactorily. The results are in keeping with an atomic binding for HCl and if the atomic character of the dissociation products be accepted it appears that the dielectric constant measurements lead indirectly to the order of magnitude of our values for $\int_0^\infty \mu(\nu)d\nu$. This lends further support to Van Vleck's criticism of that explanation of the discrepancy between the extrapolated optical and direct measurements of the dielectric constant of HCl which depends on an appeal to the infra-red vibration bands. Some aspects of the recent work on the coupling effect in gases are examined and Badger's data in the pure rotational spectrum of HCl have been studied on the assumption of a line structure derived on the basis of such "coupling" pressure broadening. The value for the line intensity found here is in slightly better agreement with the new quantum theory but the discrepancy is still excessive.

A PREVIOUS communication[1] on the results of an investigation of the HCl fundamental infra-red vibration-rotation band concerned itself primarily with the relative strengths of the band-lines for the determination of which it was not crucial to know very precisely their structure and nature, although these matters were considered at some length. It is proposed in this paper, among other things,[2] to amplify our earlier discussion of the experimental area versus tube-length curves and to take up more critically the form and breadth of the lines and their absolute intensities. Recent developments in the quantum theory have stressed the quantitative prediction of line intensities and their correlation with other experimentally

[1] D. G. Bourgin, Phys. Rev. **29**, 794, 1927. This paper will be referred to as I.

[2] D. G. Bourgin, Phys. Rev., **31**, 704 1928,

determinable magnitudes. Such information as this paper affords in the way of experimental estimates of absolute intensities is therefore expected to be of immediate application. Certain other extensions and applications of experiment will also be touched on in the course of this work.

The method of approximation developed here for the analysis of the curves of line-area versus tube-length is applicable to all similar spectroscopic investigations (*cf* for instance the application to Badger's infra-red data) in which the resolution is insufficient to permit the use of Beer's law, as well as to data obtained in other fields.

Briefly our problem may be stated as follows: $A(x)$ is supposed known for real positive x and is defined by

$$A(x)=\int_0^\infty (1-e^{-\mu(\nu)x})d\nu \tag{1}$$

We wish to determine $\mu(\nu)$ or less ambitiously to characterize it as regards certain properties. To fix our attention we may interpret $A(x)$ as the total light absorption due to the interposition of a medium of absorption coefficient $\mu(\nu)$ and thickness x between light source and receiver. If we are dealing with an absorption line we should be interested in its height $(\mu(\nu)_{\text{maximum}})$, its width defined for a singlet line as its breadth in frequency units measured for the ordinate $\mu(\nu)_{\max}/2$, and its intensity $(\int_0^\infty \mu(\nu)d\nu$ or the equivalent quantity $dA(0)/dx)$.

Some aspects of the problem have been investigated in a mathematical paper. We shall restate some of the results of that paper[3] and first we remark that if $\mu(\nu)$ satisfies certain restrictions it is possible to derive an explicit formula for $\mu(\nu)$ in terms of known functions and their integrals. This solution will not be used here, however, because of practical difficulties of application. Instead we shall discuss the implications of some qualitative theorems correlating the variation in form of $\mu(\nu)$ with the properties of $A(x)$. The practicable determination of the characteristics of $\mu(\nu)$ proceeds thus: we assume (on the basis of theory or otherwise) a certain functional form for $\mu(\nu)$ involving arbitrary parameters. The parameters are determined by comparison of $E(x)$ and $A(x)$ where the notation refers to the experimental and computed ordinates (from (1)) respectively.

Consider integrable even functions $\mu(\nu)$ which are continuous and monotone decreasing on the interval $(0,\infty)$. It is then true[3] that if the curve* $\mu_1(\nu)$ vs ν and the curve $\mu_2(\nu)$ vs ν intersect just once in the interval $(0,\infty)$ and $\mu_1(\nu)\geqq\mu_2(\nu)$ on the interval up to the point of intersection and $\mu_2(\nu)\geqq\mu_1(\nu)$ for the remainder of the interval and if $\int_0^\infty \mu_1(\nu)=\int_0^\infty \mu_2(\nu)d\nu$ then $A_2(x)>A_1(x)$, $dA_2(x)/dx>dA_1(x)/dx$ for sufficiently small positive x, and $dA_2(x)/dx<dA_1(x)/dx$ for sufficiently large x. The important characteristic of the $A_2(x)$ curve is that it has a more pronounced "bend" than the $A_1(x)$ curve, and this observation suggests the direction in which to modify a preliminary

[3] We shall refer to this paper as II. It will appear shortly in the Tokohu Mathematical Journal.

* It is suggested that the reader draw graphs to illustrate these theorems.

choice for $\mu(\nu)$ in order to attain a closer representation of a given curve. For the case of doublet lines, somewhat similar theorems are true.

The fundamental conditions on the computed functions will now be developed. Unless otherwise stated we shall materially simplify our exposition by insisting that $\mu(\nu)$ involve two parameters only and furthermore we impose the separability condition, namely, that there exists a transformation defined by

$$z=(\nu-\nu_0)f(\alpha,\beta) \tag{1.1}$$

such that

$$\begin{aligned}\mu(\nu)&\equiv\mu(\nu-\nu_0,\alpha,\beta)\\&=F(\alpha,\beta)\phi(z)\end{aligned} \tag{1.2}$$

where the notation indicates that α and β do not occur explicitly in $\phi(z)$.

Our approximation method assumes

$$E(x)=[1/f(\alpha,\beta)]\int_{-\nu_0}^{\infty}(1-e^{-F(\alpha,\beta)x\phi(z)})dz \tag{1.3}$$

The lower limit may generally be replaced by $-\infty$ and on introducing n to designate the product $xF(\alpha,\beta)$ we obtain

$$E(x)f(\alpha,\beta)=\int_{-\infty}^{\infty}(1-e^{-n\phi(z)})dz=A(n) \tag{1.4}$$

Clearly the evaluation of $A(n)$ does not involve knowledge of the parameters. It is evident from Eq. (1.4) that the curve for $E(x)$ vs. x is derivable from the curve for $A(n)$ vs. n by appropriate linear modification in the scale of n and $A(n)$ (i.e., an affine transformation). We now indicate two methods of testing the adequacy of an assumed $\mu(\nu)$.

Suppose, that $\mu_1(\nu)$ leads to a perfect representation of the $E(x)$ vs. x curve in the sense that the computed $A(n)$ vs. n curve is transformable into the $E(x)$ vs. x curve by an affine transformation. We must have

$$E(x_1)/A(n_1)=E(x_2)/A(n_2) \tag{2}$$

subject to the condition $x_1/n_1=x_2/n_2=\lambda$. Writing $x_2=x_1+\Delta x$ and $n_2=n_1+\Delta n$ and noting that $\Delta x/\Delta n=\lambda$ we infer

$$\frac{A(n+\Delta n)-A(n)}{A(n)\Delta n}=\frac{E(x+\Delta x)-E(x)}{\lambda E(x)\Delta x} \tag{2.1}$$

$$\frac{A(n)x(dE(x)/dx)}{E(x)n(dA(n)/dn)}=1 \tag{2.11}$$

This may also be written

$$\frac{d\log E(x)}{d\log x}-\frac{d\log A(n)}{d\log n}=0 \tag{2.12}$$

The relation 2.12 (or 2.11) is fundamental to the theory and because of its independence of scale factors indicates immediately whether or not a given type of $\mu(\nu)$ is adequate. One plots $d \log E(x)/d \log x$ vs. x and $d \log A(n)/d \log n$ vs. n on the same graph paper—for perfect representation the graphs should coincide throughout. An alternative method of testing an assumed form of $\mu(\nu)$ is to determine the transformation $n=\lambda x$, $Y=A(n)/\rho$ required to make the curve $y=Y(x)$ coincide with the experimental curve $y=E(x)$ at two arbitrary points x_1 and x_2 and then to compare the corresponding complete curves. To fix λ we have only to solve graphically the equation

$$A(\lambda x_1)/A(\lambda x_2)=E(x_1)/E(x_2)$$

Then ρ is determined by

$$A(\lambda x_1)/\rho \equiv Y(x_1)=E(x_1)$$

If the curve $y=Y(x)$ agrees with the curve $y=E(x)$ within the limits of experimental error throughout the range of observation, we may compute the corresponding integral absorption coefficient α from

$$\alpha \equiv \int_0^\infty \mu(\nu)d\nu=(dY/dx)_{x=0}=(1/\rho\lambda)(dA/dn)_{n=0} \tag{2.4}$$

The uncertainty in the determination of α will evidently be compounded of the uncertainty regarding the correct form of $\mu(\nu)$ and the uncertainty in the determination of $\rho\lambda$. In the absence of a rigorous theory of line

TABLE I. *Tabulated values of the fundamental approximating functions.*

n	$\psi_D(n)$	$\psi_S(n)$	$\psi_L(n)$	n	$\psi_D(n)$	$\psi_S(n)$	$\psi_L(n)$
.1		0.1562	0.1532	1.	0.6415	1.494	1.26
.2		0.315	0.2984	2.	0.9812	2.845	2.09
.3				3.	1.1692	4.0527	
.4				4.	1.3175		
.5	0.378	0.807	0.699	5.	1.4115	6.2	3.69
.6				6.			
.7				7.			
.8				8.			
.9				9.			
				10.		9.127	52.7
				50.			12.4

broadening free from arbitrary assumptions, we can only estimate the uncertainty in α due to uncertainty regarding the form of $\mu(\nu)$ by trying several different forms for the function $\mu(\nu)$ and observing the variation in α for those forms which fit the empirical data adequately. The fractional uncertainty in α due to uncertainty in the determination of $\rho\lambda$ is easily calculated from the uncertainties M_1 and M_2 in the values of the experimental absorption $E(x_1)$ and $E(x_2)$. It has the value

$$\left|\frac{\delta\alpha}{\alpha}\right| = \left|\begin{matrix} |M_2| & |[n_1A'(n_1)-A(n_1)]| \\ -|M_1| & |[n_2A'(n_2)-A(n_2)]| \end{matrix}\right| \div \rho \left|\begin{matrix} A(n_2) & n_2A'(n_2) \\ A(n_1) & n_1A'(n_1) \end{matrix}\right|$$

where $n_1=\lambda x_1$; $n_2=\lambda x_2$; $A'(n_1)=(dA/dn)_{n=n_1}$; $A'(n_2)=(dA/dn)_{n=n_2}$.

This, of course, is an upper limit to the uncertainty in α since in practice the curve $y=A(\lambda x)/\rho$ must fit the experimental curve within its limits of error not only at the points x_1 and x_2, but throughout the range of observation. The application of Eq. (2.5) to the computations of the HCl fundamental band is given on page 246.

We shall now systematically investigate some rather important forms for $\mu(\nu)$. The first function to be considered is that giving the line-shape of an originally infinitesimally thick line on the assumption of a Doppler broadening.

$$\mu_D(\nu) = Pe^{-c(\nu-\nu_0)^2} \tag{3}$$

(From another point of view this is merely the error curve in ν units.) Since ν_0 is generally very large we may write the total absorption in the form

$$A(x) = \int_0^\infty \{1-\exp[-xPe^{-c(\nu-\nu_0)^2}]\}d\nu \tag{3.1}$$

A simple transformation allows us to write

$$A(x) = (2/c^{1/2})\int_0^\infty \{1-\exp[-ne^{-z^2}]\}dz = (2/c^{1/2})\psi_D(n) \tag{3.2}$$

where $n=Px$. $\psi_D(n)$ is calculated in Table I for sufficient values of n to make an accurate graph possible. For large n values a method of graphical integration[5] was used. For small values of n the results were checked by evaluation of the series

$$\psi_D(n) = (\pi^{1/2}/2)\sum(-1)^{N-1}n^N/N!N^{1/2} \tag{3.3}$$

or

$$\psi_D(n) = 0.8862\{n-0.35355n^2+0.096225n^3-.02083n^4+.00285n^5\} \tag{3.31}$$

The peak height, breadth and intensity for this line structure are respectively P, $(\log 4/c)^{1/2}$, $P\ (\pi/c)^{1/2}$.

It will be noticed that the line intensity may be expressed as $cnA(x)/x\psi(n)$. We shall refer to this result as Theorem A and it may be shown without difficulty that this is always the case provided $\mu(\nu)$ involves the parameters α and β separably even if $\mu(\nu)$ contains x provided* only that $(\partial/\partial x)\int_0^\infty \mu(\nu)d\nu = 0$. In this latter case, however, although the ratio $A(x)/\psi(n)$ occurs, the approximating function is not $\psi(n)$ but $\psi(n)/f(\alpha,\beta,\lambda(n,\alpha,\beta))$ where $f(\alpha,\beta,x)$ is

[5] $\psi_D(n)$ was written as $\int_0^1(1-\exp[-ne^{-z^2}])dz+\int_0^1(1-\exp[-ne^{-1/z^2}]dz/z^2$ and the area under the integral curves was obtained by counting squares.

* This is the case, for instance, for pressure broadening (see p. 243).

the analogue of $f(\alpha,\beta)$ Eq. (1.1) and $\lambda(n,\alpha,\beta)$ is the value of x expressed in terms of n, α and β.

The next line-shape to be taken up is that suggested by a consideration of a Stark broadening[6] of an absorption line induced by the presence of neighboring molecules. On using Holtsmark's expression[7] for the probability that a given field exist at a point and the assumption of a uniform shift dependent on the square of the molecular field, the author has derived

$$\mu(\nu) = k(\nu/c)^{1/2}/c(1+\nu/c)^2 \tag{4}$$

$$A(x) = c\int_0^\infty (1-e^{-nz^{1/2}/(1+z)^2})dz = c\psi_S(n)$$

where $n = kx/2c$. The values of $\psi_S(n)$ given in Table I were evaluated for small n from the series

$$\psi_S(n) = 2n\left[\frac{\pi}{4} - \frac{n}{2!}\frac{1}{12} + \frac{n^2}{256}\frac{\pi}{4} - \frac{n^3}{3!}\frac{1}{210} - \frac{55\pi n^4}{(65536)^2}\right. \tag{4.1}$$

$$= 1.5708n - 0.0825n^2 + 0.0061359n^3 - 0.000397n^4$$
$$- 0.00002197n^5 \tag{4.11}$$

These values are closely the same as those determined by a graphical integration[8] by means of which the tabulation was extended to higher n values.

Peak absorption takes place for $\nu = c/3$. The width is obtained by solving for the difference of the two positive roots of $\mu(\nu)_{\max}/2 = (k/4c)(\nu/c)^{1/2}/(1+\nu/c)^2$. This turns out to be 1.8937 c. The asymmetry of the curve is so pronounced that the width affords only slight information about the true curve form. The integrated absorption coefficient is $n\pi A(x)/2x\psi_S(n)$ or $\pi kc/4$.

For completeness[1] the results for the line-shape predicted by theories depending on finite wave train emission (or absorption), for instance, the collision interruption of emission as postulated by Lorentz, are also given. Here

$$\mu(\nu) = a/[(\nu-\nu_0)^2+b^2] \tag{5}$$

We readily derive

$$A(x) = 2b\psi_L(n) \tag{5.1}$$

where

$$\psi_L(n) = \pi\left\{\frac{n}{2} - \frac{2n^2}{8} + \frac{n^3}{32} - \frac{5n^4}{768} + \frac{7n^5}{6144} - \cdots\right\} \tag{5.2}$$

[6] The derivation is somewhat long and is omitted, inasmuch as the type of curve does not fit the HCl data. Professor E. C. Kemble has remarked to the writer that the inadequacy of the Stark effect curves is evident *a priori* from the fact that the HCl lines show no pressure shift.

[7] J. Holtsmark, Ann. d. Physik, **58**, p. 677 (1919).

[8] The graphical integration depends on the representation of $\psi(n_S)$ in the form

$$2\int_0^1 (1-e^{-nz^{1/2}/(1+z)^2})dz + 4\int_0^1 (1-e^{-nz_1^2/(1+z_1^2)^2})dz_1/z_1^2.$$

In some investigations the data correspond to increase of pressure rather than gas-column length. Admixture of foreign gases is found to be far less effective in modifying line-shape than addition of the absorbing gas. Formally, this may be taken account of on the Lorentz theory by presupposing a large difference in the diameter of a molecule depending on whether its neighbors are of the same or different types; however it seems desirable to consider theories which connect up more intimately the nature of the added gas and the resultant change in line-shape. The application in this paper will be to Badger's ultra-red work. In order to establish plausible formulae we advert to some work on atomic spectra. Two recent papers have taken up the problem of the coupling, or resonance effect, of atoms in similar quantum states, under the idealization of no temperature agitation. Mensing,[9] using quantum-theoretic ideas, has derived the perturbation function on the assumption that only two molecules are involved, while Holtsmark[10] considers a set of classical oscillators vibrating parallel to the electric vector of the incident wave and determines the set of fundamental frequencies of this system. Mensing derives a line-breadth dependent on N (the number of atoms, or molecules, per cc) while Holtsmark finds that the variation is proportional to $N^{1/2}$. (Schuetz[11] confirms Holtsmark's line-breadth variation in the case of Na absorption, but in view of the extreme simplications introduced it is hardly likely that either treatment is quantitatively correct.)

It has been urged by commentators as a basic objection, that the time of passage of one atom through the sphere of action of another is of the order of 10^{-12} seconds, which is infinitesimal in comparison with the usual mean life of 10^{-8} seconds and hence that the resonance effect is insignificant. It seems plausible, however, that the criterion to be applied is rather that of the number of periods during which appreciable influence is exerted. For atomic frequencies this is of the order of 10^3 or greater, though for slow molecular rotation the value is very much less. For instance, the lower rotational states of HCl have a frequency of about 10^{12} so that there may be a real objection to extending the coupling concept to the ultra-red rotation bands.

As a possible refinement of the treatment (particularly Holtsmark's) it seems suggestive to approximate the effect of the short coupling interval by subjecting the neighboring atoms to arbitrary phase shifts with a random distribution in time and it is hoped to present results on this extension at some later time.

If an error-curve line-structure be assumed we expect

$$\mu_p(\nu) = Pe^{-\alpha(\Delta\nu)^2/p^s}/p^{(s-2)/2}$$

[9] L. Mensing, Zeits. f. Physik, **34,** p. 611 (1925).

[10] T. Holtsmark, Zeits. f. Physik, **34,** p. 122 (1925).

[11] Schuetz, Zeits. f. Physik, **34,** p. 122 (1925). Schuetz objects to Holtsmark's results because of the Gaussian error curve form of absorption line. However, this line structure is not inherent in Holtsmark's derivation which merely leads to a mean square value of the frequency shift dependent on N.

where $s=1$ for Holtsmark's conclusion and 2 for that of Mensing. The form of $\mu_p(\nu)$ is easily checked when it is remembered that the intensity is a linear function of the number of mol./cc and hence of the pressure and that the mean square value of $\Delta\nu$ is to be proportional to N^s.

This $\mu(\nu)$ satisfies all the conditions of Theorem A and it is obvious that $\psi(n)$ is our previously tabulated $\psi_D(n)$. Therefore

$$\int_0^\infty \mu(\nu)d\nu = \pi n A(p)/2p\psi_D(n) \tag{6.1}$$

For $s=1$, $n=Pp^{3/2}$ and it is immediately corroborated that our approximating function is $n^{1/3}\psi_D(n)$ and that $A(p)=2n^{1/3}\psi_D(n)/P^{1/3}\alpha^{1/2}$.

The alternative assumption $s=2$ implies an approximation function of the form $n\psi_D(n)$. It may be remarked in passing that though Holtsmark's theory is not extensible[12] to a frequency distribution of the type $\mu_L(\nu)$, the interpretation[13] of the constants in the Lorentz theory yields the pressure broadening formula

$$\mu(\nu)=\frac{\alpha p^2}{(\nu-\nu_0)^2+\beta^2p^2} \tag{7}$$

It does not seem possible to approximate doublet lines easily by the method of this paper. We may characterize the difficulty by the observation that the line shapes for different values of the separations of the components are not similar, or put otherwise that it is not possible to separate the parameters so as to permit of reducing all curves to the same normal form by an affine transformation.[14] The determination of the parameters by a method of successive approximation would in general be tedious. Reducible cases arise for very small or very large doublet separations. For the first circumstances we use the singlet structure; for the latter we write

$$\mu(\nu)=\mu_1(\nu-\nu_1)+\mu_2(\nu-\nu_2) \tag{8}$$

and since $\nu_2-\nu_1$ is assumed very large we have

$$A(x)=\int_0^\infty \{2-e^{-\mu_1(\nu)x}-e^{-\mu_2(\nu)x}\}\,d\nu \tag{8.1}$$

[12] Inasmuch as the mean square value of $\Delta\nu$ is infinite.

[13] Lorentz' derivation makes it clear that b(cf. Eq. 5) is linear in N and therefore p, and the condition that the intensity be linear in N determines the quadratic dependence of a on p.

[14] Consider for example the doublet line given by

$$\mu(\nu)=P\left\{\frac{k}{(\nu-\nu_1)^2+b^2}+\frac{1-k}{(\nu-\nu_2)^2+b^2}\right\}$$

where ν_1, ν_2 and k are usually known. We might reduce this to

$$\mu(\nu)=f(P,b)\left\{\frac{k}{z^2+1}+\frac{1-k}{[z-(\nu_2-\nu_1)/b]^2+1}\right\}$$

or some similar form but it is not possible to write this as $f(P,b)\,\phi(z)$.

Using the subscript T to indicate an infinitely separated doublet structure, there results

$$\psi_T(n)=\psi(kn)+\psi((1-k)n) \quad 0<k<1 \tag{8.11}$$

so that we may get the $\psi_T(n)$ functions directly for each of the line shapes from the tabulated singlet line functions of Table I.

Some of the special line structures taken up above will first be applied to the author's data on the fundamental band of HCl. Table II gives the numerical values deduced for each of the line types including the Lorentz collision broadened line for which the results have already been published.

TABLE II. *Comparative calculations for the HCl fundamental band.*

	$\psi_D(n)$	$\psi_S(n)$	$\psi_L(n)$	$\psi_{DT}(n)$	$\psi_{LT}(n)$
$\int_0^\infty \mu(\nu)d\nu$	40.06×10^{10}	33.7×10^{10}	45.5×10^{10}	40.9×10^{10}	37.7×10^{10}
Width	7.479×10^{10}	2.1×10^{11}	2.3×10^{10}		
Width each component					1.2×10^{10}
$dp(r_0)/dr$	0.89×10^{10}		0.888×10^{10}	0.84×10^{10}	0.836×10^{10}
A_{01}	38		40	38	39
B_{01}	84 $\times10^{14}$		96 $\times10^{14}$	85 $\times10^{14}$	84 $\times10^{14}$

In order to obtain an indication of the direction of modification required by a consideration of the isotope doubling, an approximation was made using the assumption of infinite component separation (i.e., $\psi_T(n)$) and the known isotope distribution, 77:23. The line intensities calculated for the error curve and the Lorentz line doublets are somewhat less than the value obtained for an assumed singlet structure. It seems plausible to expect that an approximation function, based on a finite doublet separation would yield constants intermediate between those calculated by means of the $\psi(n)$ and $\psi_T(n)$ curves.

Fig. 1 is indicative of the degree of accuracy with which the various line shapes are capable of representing the experimental data. The curves are the graphs of the functions $A(x)$ for the lines $M=2$, 3, 4 where the ordinate scales have been adjusted so that the various curves are superposed as nearly as possible (actually it is clear that a slight reduction in the ordinate scale for the lines $M=2, 4$ would bring the three curves in much closer coincidence). It is evident that there is but slight variation in the experimentally determined total absorption-curve shape. The attempt was made to approximate the line $M=3$ most closely. It will be observed that the deviation of the computed points is small and also that practically all the computed points are below the corresponding point on the experimental curve for short tube-lengths; hence it is possible that our estimates[15] for $\int_0^\infty \mu(\nu)d\nu$ may be somewhat low. The approximation by the Stark curve

[15] Slightly more accurate values for the points on the $\psi_L(n)$ curve account for the fact that this paper's estimate of $\int_0^\infty \mu_L(\nu)d\nu$ is somewhat lower than that given in I.

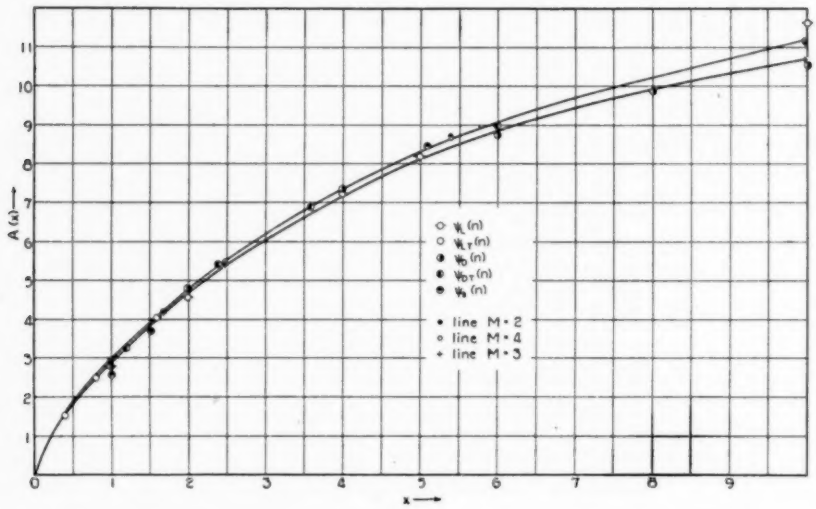


Fig. 1. Comparison of experimental and computed total absorption.

is decidedly forced and hence not plausible. There are objections to the Doppler structure. The theoretical expression for a Doppler line has often been derived on the basis of kinetic theory considerations in the form

$$\mu(\nu) = P(\lambda, T \cdots) e^{-m\lambda_0^2(\Delta\nu)^2/2kT} \tag{9}$$

The broadening given by Eq. (9) is about 1.76A as against the value 24.7A calculated from the fitting of the experimental curve by $\psi_D(n)$. Of course it is still possible that the true line shape has the characteristics of an error curve even though the Doppler explanation is invalid.

The Lorentz curve taking into account the doublet structure seems to provide a fairly faithful delineation of the absorption line. The breadths calculated for the components of the Lorentz line are of the order of 10^{10} frequency units which is about half that obtained on the assumption of a singlet line and only some three times the width expected theoretically on the basis of a Doppler widening (assuming the constants for the infinitely separated structure). The indications are, therefore, that a more refined test would favor the superposition of a Doppler broadening on a dispersion-curve pattern.

Two important questions, which can be answered only partially here are, (A) the variation possible in the integrated absorption coefficient computed from a given line pattern; (B) the range of variation of the estimates of the intensities as derived from various line shapes.

Eq. (2.5) assigns an upper bound to the differences contemplated in (A). A rough calculation based on an approximation by means of the $\psi_L(n)$ curve using the values $M=6$ for $x=1$ cm and $M=1$ for $x=0.1$ cm indicates a maximum inaccuracy of about 8 percent. As regards the possibility of widely divergent estimates of intensity for different line types, we may reason plausibly from the results tabulated in Table II. Of the five line

shapes investigated, the four that fit the observations adequately yield estimates whose maximum deviation from each other is about 20 percent and whose deviation from the mean value is about 10 percent. The values yielded by the Stark curve are useful as suggesting limiting values for the possible deviations since this curve is so decidedly inferior as to be really incompatible with the experimental evidence. Nevertheless, even here the intensity is only some 20 percent lower than the mean and 30 percent lower than the maximum recorded computed intensity.

Our expectation is, therefore, that the approximation method yields results correct within 20 percent. When allowance is made for unavoidable experimental error (cf. I) it appears that 30 percent is a fair estimate for the accuracy of the absolute intensities.

Dennison[16] has recently presented a carefully worked out theory of line broadening. Without prejudicing the merit of his independent derivation it may be pointed out that this theory may be shown to be closely akin to that of Lorentz and leads, in fact, to the same expression for the line structure, namely, $\mu_L(\nu)$ (cf Eq. (5))—moreover, except for a difference in the value of a numerical constant the theoretical interpretations of a and b are identical with those which may easily be derived from Lorentz's work, i.e.,

$$b = kN\sigma^2/(hm)^{1/2}\ ;\quad a = \int_0^\infty \mu(\nu)d\nu = b/\pi \tag{10}$$

where the usual kinetic theory notation has been adhered to and the constant k has the value $k_L \equiv (8/\pi)^{1/2}$ in Lorentz's work and $k_D \equiv (7/4\pi)^{1/2}$ in Dennison's.

It does not seem that Dennison noticed this close relationship between his results and those of Lorentz and that therefore his demonstration of the adequacy[17] of his expression for $\mu(\nu)$ to represent the author's data is already contained in the writer's use of $\mu_L(\nu)$ in I. A comparison of Dennison's values for the total absorption as computed from Paton's data on a 4 cm tube shows that they are in excellent agreement with the writer's absorptions for short tubes (except possibly with the least reliable of the writer's measurements, namely, those for the 2.97 cm tube).

The knowledge of b or a enables us to estimate the effective molecular diameter σ and it is clear that the ratio of the Lorentz to the Dennison value will be $(k_D/k_L)^{1/2} = 2+$. This expectation is, in fact, substantiated by a direct calculation which gives $\sigma_L = 4.5 \times 10^{-8}$ cm whereas Dennison's value (also based on the writer's values for $\int_0^\infty \mu(\nu)d\nu$) is $10.6\ 10^{-8}$ cm. The fact that kinetic theory estimates support the Lorentz value may perhaps be construed as deciding between Dennison's and Lorentz's analysis, but it is, of

[16] D. M. Dennison, Phys. Rev. **31**, 501, 1928

[17] From our point of view Dennison's demonstration amounts to recomputing the author's approximation function ($2b\psi_L(n)$) using the value of $\int_0^\infty \mu(\nu)d\nu$ derived by use of it and showing that it really does represent the experimental total absorption curve closely.

course, to be borne in mind that any collision broadening theory is necessarily only a qualitative guide.

It seems of importance to discuss the plausibility of the estimates of the characteristic constants associated with HCl which we have derived here. For this purpose we investigate the nature of the variation of the electrical moment $p(r)$ and effective charge $q(r)=p(r)/r$. We write

$$p(r)-p(r_0)=\frac{dp(r_0)}{dr}(r-r_0)+\frac{1}{2}\frac{d^2p(r_0)}{dr^2}(r-r_0)^2+\cdots$$

$$q(r)r-q(r_0)r_0=\left[\frac{dq(r_0)}{dr}r_0+q(r_0)\right](r-r_0)+\cdots \tag{11}$$

where r_0 refers to equilibrium position.

For the calculations of $dp(r_0)/dr$ given in Table II it was assumed that $(r-r_0)$ was harmonic[18] in t and the formulae used were based on Oppenheimer's quantum matrix expressions for the intensity of transition.[19] The most natural assumption[20] to make about HCl is that on adiabatic separation of the nuclei we should obtain H^+ and Cl^-. Hence it might seem plausible that $dq(r_0)/dr>0$ or by Eq. (11), $dp(r_0)/dr>q(r_0)$. The new quantum theory expression applied to Zahn's data on the dielectric constant of HCl leads[21] to $q(r_0)=0.818\times10^{10}$ which is practically equal to our value of[22] 0.86×10^{10} for $dp(r_0)/dr$. Since the precision limits of the integrated absorption coefficients are 25 percent or poorer it is even possible[23] that $dp(r_0)/dr<q(r_0)$ which would imply that adiabatic separation results in neutral H and Cl. We may say here only that $dq(r_0)/dr$ is not large.

A small positive value of $dq(r_0)/dr$ is also reconcilable with a separation into neutral atoms for, since the equilibrium position of the H nucleus is within the outer Cl shell, it may be that $dq(r)/dr$ becomes negative for r appreciably greater than r_0 only. It is pertinent to note the assignment of an atomic binding to HCl by Franck and Kuhn[24] on the basis of the nature of the dissociation as indicated by the absorption band limits.

[18] It may be shown that departure from the sine form would introduce higher order r derivatives of $p(r)$ and $q(r)$ in the relation between intensity and time rate of change of moment.

[19] J. R. Oppenheimer, Proc. Camb. Phil. Soc. **23**, 237 (1926). Cf. in this connection I, and Dennison's paper (reference 16).

[20] See for example E. C. Kemble, Journ. Opt. Soc. **12**, 1 (1926).

[21] Really because of the half quantum of vibrational energy in the zero state the notation $q(r_0)$ refers to the value of q for a larger value of r than r_0.

[22] The value of 0.86×10^{10} is not very different from that given in I. Dennison's recently published value of 0.95×10^{10} is based on the values of $\int_0^\infty\mu(\nu)d\nu$ given in I (which we have modified somewhat in this paper) and on a formal average of the absorption results for the various lines. The mean value is, however, not significant for the experimental measurements were capable of far greater precision in the cases of the lines $M=2$, 3, 4 than in any of the others.

[23] There are, of course, also the possibilities that our assumed line patterns were inapplicable or over-simplified or that there is some incorrectness in the theoretical formulae or physical constants used in determining $dp(r_0)/dr$ from $\int_0^\infty\mu(\nu)d\nu$.

[24] J. Franck and H. Kuhn, Zeits. f. Physik, **43**, 164 (1927).

Hence the value of $dp(r_0)/dr$ to be expected from the dielectric constant data is of the order of, or at most not very much greater than, $q(r_0)$, and is therefore in agreement with the estimates of $dp(r_0)/dr$ (and therefore of $\int_0^\infty \mu(\nu)d\nu$) given here. In this connection it is interesting to recall Van Vleck's test[25] of the suggested explanation for the incompatibility of the values of $\epsilon-1$ derived from optical data and dielectric constant measurements (namely the assumption that the consideration of the vibrational infra-red bands would bring the estimates into agreement). Actual computation, using the writer's value of $dp(r_0)/dr$ showed that the correction was far too small. The preceding discussion seems to dispose of the possibility that this value of $dp(r_0)/dr$ can be much too low[26] and supports Van Vleck's criticism.

We shall now take up Badger's[27] recent measurements on the rotation spectrum of HCl in the far infra-red. Inasmuch as Badger's findings are out of accord with theory, it seems of importance to see whether use of the more refined approximation methods described here may not indicate a fault in the working up of the data rather than in the data themselves. The approximation making use of the $n\psi_D(n)$ curve[28] yielded for the tangent at zero pressure the value 1.312×10^{-4} cm per cm of Hg pressure for a tube 77 cm long. Badger's computation gave 1.12×10^{-4} cm. The difference, though in the right direction, is too small to appreciably minimize the disagreement between theory and experiment.

It would no doubt be of value to apply the approximation methods illustrated above to the recalculation of the results of many other researches, for instance, to the determination of the intensities and intensity ratios of the Na doublets[29] (or Li or Cs, etc.). Here most of the data are for pressure variation and approximation functions of the form $n^s\psi(n)$ would lead to useful conclusions. In view of the contradictory nature of the many published results it would seem desirable to carry out an investigation for variable tube-length, since the interpretation then becomes somewhat simpler.

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February 12, 1928.

[25] J. H. Van Vleck, Phys. Rev. **30**, 31 (1927).

[26] Certainly it is most unlikely that there is some unrecognized error in the data or deductions large enough to account for $dp(r_0)/dr$ being too small by a factor of 100.

[27] R. M. Badger, Proc. Nat. Acad. Sci. 408, 13 (1927). Note added July 9, 1928. In a recent conversation Dr. Badger mentioned unpublished work on NH_3 as supporting the view of a real difference between experimental intensities in the ultra-red and the predictions of existent theory.

[28] But see the remarks on p. 243.

[29] C. Fuchtbauer, Phys. Zeits. **12**, 722 (1911); R. Ladenburg, R. Minkowski, Zeits. f. Physik **6**, 153 (1921); B. Trumpy, Zeits. f. Physik **34**, 714 (1925), **40**, 594 (1926); W. Orthmann, Ann. d. Physik **78**, 607 (1925); W. Schutz, Zeits. f. Physik **25**, 299 (1924), etc.

ON THE QUANTUM MECHANICS OF THE ROTATIONAL DISTORTION OF MULTIPLETS IN MOLECULAR SPECTRA

By E. Hill and J. H. Van Vleck

Abstract

Most of the paper is on the effect of molecular rotation on spin multiplets, but the last section 5 considers the rather different subject of "σ-type doubling."

1. **Hund's limiting cases (a) and (b),** those commonly considered, are realized when the coupling between the electronic spin and the molecular axis of figure is very strong or very weak. Preparatory to the new analysis for the intermediate case, amplitude matrices are given both for cases (a) and (b), including phase factors in (b).

2. **The general intermediate case** can be handled (except for purely algebraic difficulties) both for frequencies and intensities by our mathematical method. The procedure is to start with case (b) and to introduce a coupling energy which is proportional to the cosine of the angle between the axis of electronic spin s and the molecular axis of figure, and which when increased adaibatically converts the system over into case (a). The formula for the energy W is the solution of an algebraic equation of order $2s+1$. Approximate solutions are given for nearly case (b) with any s and for nearly case (a) in triplet spectra ($s=1$).

3. **The doublet case** ($s=\frac{1}{2}$) is particularly satisfactory as (unlike the old quantum theory) the analysis yields a simple closed formula for the energy, viz.,

$$W=\left[(j+\tfrac{1}{2})^2-\sigma_k^2\pm\tfrac{1}{2}\left\{4(j+\tfrac{1}{2})^2+\lambda(\lambda-4)\sigma_k^2\right\}^{1/2}\right](h^2/8\pi^2I)$$

which holds throughout the interval from (a) to (b) both for regular and inverted multiplets. Here λ is an abbreviation for $8\pi^2AI/h^2$, where A is the proportionality factor in the magnetic coupling energy $As\cdot\sigma_k$. This formula yields an adiabatic correlation of energy levels in case (a) with those in case (b) which is precisely that predicted by Hund and Kemble including the anomalous behavior of the component $j=\sigma_k-1/2$ in "regular" multiplets ($A>0$). The agreement with the experimental doublet widths in the OH band 2811 is slightly better than in the old quantum theory. Intensity formulas are given which apply throughout the range from (a) to (b). Here account is taken of the fact that the moment of inertia I and coupling constant A are different in the initial and final states if there are changes in "electronic" quantum numbers.

4. **Simple special cases of the doublet intensity formulas** arise when there is (a) type coupling in the initial states and (b) in the final or vice versa. The $^2P\rightarrow{}^2S$ bands usually meet this condition and formulas for them are developed; the main new result is that for a given initial state the transitions ending on $j_k=j-1/2$ and $j_k=j+1/2$ are of equal intensity. As another illustration intensity formulas are given for $^2D_a\rightarrow{}^2P_b$.

5. **An elementary theory of σ-type doubling** is developed by using mathematics very similar to that in the preceding but introducing adiabatically a coupling proportional to the *square* rather than first power of the cosine of the angle between an angular momentum vector k and a "core" consisting of the non-gyroscopic "dumb-bell" molecular model. In a stationary molecule the sign of σ is arbitrary and if $\sigma\neq0$ there are two states of identical energies. It is shown that actually the rotation removes this degeneracy and creates a small splitting into two levels for a given value of σ^2 which Mulliken calls "σ-type doubling." Kronig's result is obtained that the doubling is smaller for large σ^2. The combination relations predicted by Hulthén and treated mathematically by Kronig are shown to apply exactly even when the perturbing effect of the angular momentum perpendicular to the figure axis in case (a) is considered, and the coupling is no longer rigorously of type (a). Interaction of σ-type degeneracy with the spin is reserved for a later paper, so section 5 applies primarily to singlets.

IN HIS important recent work, Hund[1] has introduced the concept of the spin electron into the theory of the spectra of diatomic molecules, and has concluded that the spectral terms of a given molecule can be classed in one or another of a number of groups which he calls case (a), case (b), etc. These cases correspond to special limiting molecular configurations occurring for particular asymptotic values of the molecular rotational energy relative to the energy of interaction between the spin axis and the rest of the molecule; e.g., for very tight coupling of the spin axis the motion is that of case (a), while for very weak coupling it may be that of case (b).

The purpose of the present paper is to give frequency and intensity formulae, for diatomic molecules, applicable to the transition stage intermediate between these limiting cases, which are the only ones ordinarily considered. The initial step in this direction has been taken by Kemble.[2] Using the methods of the old quantum theory, he derived energy formulas which are applicable over certain portions of the transition range from case (a) to case (b), and which give good agreement with the experimental data in the case of the OH band λ2811. The treatment of the problem by the new quantum mechanics, which we give in the present paper, has the advantage of yielding a simple frequency formula for the doublet case, as well as exact expressions for the intensities.

1. The Limiting Cases (a) and (b)

The present section will summarize information about the limiting cases (a) and (b) which is to a considerable extent not entirely new, but which is prerequisite to the mathematical treatment of the intermediate case.

Common features of (a) *and* (b). In either case the effective component of electronic angular momentum is a vector $\mathfrak{o}_k$ directed along the axis of symmetry of the molecule. Here and throughout the article, expressions printed in boldface type are vector matrices. Angular momentum is throughout measured in multiples of the quantum unit $h/2\pi$, so that by an angular momentum $\sigma_k=1$ for instance, we mean really an amount $h/2\pi$, etc. The resultant spin angular momentum of all the electrons in the molecule is given by the vector $\mathbf{s}$, the elements of $\mathbf{s}^2$ being $s(s+1)$. In case there is more than one valence electron we assume the behavior characteristic of "normal multiplets," viz., that the spins $s_\tau=\frac{1}{2}$ of the individual electrons are coupled together to form a quantized resultant $\mathbf{s}$. This assumption seems to be justified by the empirical facts of molecular spectra, as well as by the dy-

[1] F. Hund, Zeits. f. Physik **36**, 657 (1926). Cf. also the two later papers: Zeits. f. Physik **40**, 742 (1927), and Zeits. f. Physik **42**, 93 (1927).

For a very good qualitative discussion of Hund's theory, cf. E. C. Kemble, "Molecular Spectra in Gases," Chap. VII, sec. 5, Bull. Natl. Research Council, **57**, (1926). For extensive discussions of cases (a) and (b) particularly with reference to the experimental data on band spectra, cf. R. S. Mulliken, Phys. Rev. **29**, 637 (1927); Phys. Rev. **30**, 138 (1927); Phys. Rev. **30**, 785 (1927). The notation used in this paper is the same as that of Mulliken.

[2] E. C. Kemble, Phys. Rev. **30**, 387 (1927).

namics of the situation.[3] Spectroscopists classify terms as S, P, D, F states according as $\sigma_k=0, 1, 2, 3$, and further, the spectra are singlets, doublets, triplets, according as $s=0, \frac{1}{2}, 1, \cdots$. The total angular momentum of the molecule is always given by the vector j, and its projection in the direction of spacial quantization yields the magnetic quantum number m, which has the range of values $m=-j, -(j-1), \cdots, j$.

As customary, we have neglected the component of electronic orbital angular momentum perpendicular to the axis of symmetry of the molecule. The justification for doing this is that due to the rapid precession of the orbital angular momentum k about the axis of figure, the elements of the perpendicular component are of the "high frequency type" which disappear on averaging over the "electronic frequencies" and need not be considered in calculating the important perturbative terms. Also we neglect what Mulliken calls "σ-type doubling"; i.e., a hyper-doubling of the multiplet components when $\sigma \neq 0$, although at the end of the article there is a rather detached section on σ-type doubling in the absence of internal spins (i.e singlet spectra). Such doubling arises from the Heisenberg resonance effect associated with the fact that the states $-\sigma$ and $+\sigma$ have the same energy if one neglects the interaction between the rotation and the component of electronic angular momentum perpendicular to the axis of figure. This effect, however, has only a subordinate influence on the energy, as the width of σ-type doublets is small compared to the spin multiplet structures, and so we are justified in relegating it to a neglected higher order approximation.[4]

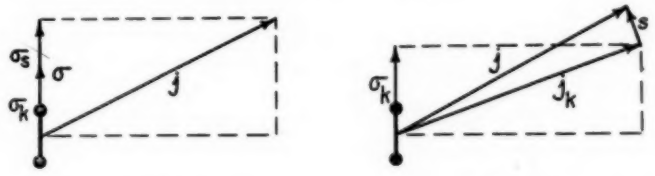
Distinction between cases (a) *and* (b). In case (a) there is a strong interaction, essentially of a magnetic nature,[5] between $\mathbf{s}$ and $\mathbf{\delta}_k$, and the former precesses rapidly about the latter; i.e., about the axis of symmetry of the molecule, to which the spin is thus tightly coupled. This involves a quantization of the projection $\mathbf{\delta}_s$ of $\mathbf{s}$ in the direction of the axis of figure, and thus introduces the quantum number σ_s which takes on the values $-s$, $-(s-1), \cdots, s$. The total electronic angular momentum about the axis of symmetry consequently has the value $\sigma=\sigma_k+\sigma_s$.

[3] The orbital angular momentum precesses too rapidly about the axis of figure for the spins to be quantized relative to an individual k_τ or even k. For explanation as to why the s_τ form a resultant s even though the interaction between σ_k and s_τ be comparable with that among the s_τ, see Heisenberg, Zeits. f. Physik, **41**, 252 (1927).

[4] Due to the resonance involved in σ-type doubling, the component of angular momentum parallel to the axis of figure is continually changing sign, so that we can no longer suppose $\sigma_k=0, 1, 2, 3, \cdots$, but we have $\sigma_k^2=0, 1^2, 2^2, 3^2, \cdots$, for $S, P, D, F, \cdots$, terms. For the present purposes no harm is done in supposing σ_k always preserves the same sign, because the high-order resonance effects cannot appreciably influence lower order effects such as spin multiplets.

[5] According to the important recent work of Dirac, Proc. Roy. Soc., **117A**, 610 (1928); **118A**, 351 (1928) the physical concept of a "spinning" electron must not be taken too literally, for it seems to be replaceable mathematically by the condition that the Schrödinger wave equations be consistent with the restricted theory of relativity and still be linear. Curiously enough, however, for most problems it seems that the older notion of an actual spin electron will give correct results, and so the term "spin" is a convenient label for certain terms in the energy which will result even with the purely relativistic treatment.

In case (b) the forces exerted on **s** due to the molecular rotation are large compared to the interaction between **s** and $\mathfrak{H}_k$. Consequently the spin axis is loosely coupled to the rest of the molecule, and makes a constant angle only with the total angular momentum j, whereas in case (a) it did with the axis of figure of the molecule. Before introducing the spin one must first quantize the total angular momentum j_k exclusive of the spin but inclusive of both the orbital angular momentum and the angular momentum developed by rotation of the nuclei about the center of gravity. The total angular momentum j is then the resultant of j_k and **s**. On the other hand in case (a) we quantize the spin relative to a fixed molecule before introducing the rotation about the center of gravity. The types of coupling characteristic of the two cases are shown in the following figure:



Case (a) Case (b)

The range of values for the quantum number j in case (a) is $j=|\sigma|, \cdots, \infty$, whereas in (b) we have instead $j_k=|\sigma_k|, \cdots, \infty$; $j=|j_k-s|, \cdots, j_k+s$. In either case there are the selection principles $\Delta\sigma_k=0, \pm1$; $\Delta j=0, \pm1$; $\Delta m=0, \pm1$ and in case (a) $\Delta\sigma_s=0$, while in (b) $\Delta j_k=0, \pm1$. The quantum number j_k in case (b) is seen to replace the number σ_s used in (a), and the adiabatic correlation of the values of j_k and σ_s is one of the problems to be considered in the present paper.

Amplitude matrices for case (a). These elements have been given by a number of investigators,[6,7,8,9] and are essentially equivalent to the London-Hönl intensity formulas. They can be extended to include transitions in the vibrational and electronic quantum numbers by noting that the effect of these transitions is to multiply the "symmetrical top" amplitudes by a set of complex factors, $D(n, n')$,[10] where the single letter n denotes the totality of these quantum numbers. This is not to be confused with the same letter n which other writers use to denote the vibrational quantum number alone. As the experimental data on intensities in the Zeeman effect for band lines are very meager, we shall not give the complete amplitude formulas, but shall

[6] H. Hönl and F. London, Zeits. f. Physik, **33**, 803 (1925).

[7] D. M. Dennison, Phys. Rev. **28**, 318 (1926). Eq. (2) of the present paper is essentially Dennison's Eq. (25).

[8] H. Rademacher and F. Reiche, Zeits. f. Physik, **39**, 444 (1926); **41**, 453 (1927).

[9] R. de L. Kronig and I. I. Rabi, Nature, **118**, 805 (1926); Phys. Rev. **29**, 262 (1927). Cf. also Kronig, Zeits. f. Physik **45**, 458 (1927).

[10] This occurs due to the fact that the Schrödinger "Eigenfunktion" can be split into two parts, one involving only the internal coordinates of the molecule, and one involving the precession coordinates. Cf. Born and Oppenheimer, Ann. der Physik **84**, 457 (1927). Cf. also Kronig, Zeits. f. Physik **46**, 814 (1927).

give a set of quantities which are derived from them, and which are proportional to the total intensities. These quantities, which are Hermitian,[11] are defined by:

$$\begin{aligned}|\, q_a(n,\sigma_k,\sigma,j\,;\quad n',\sigma_k',\sigma',j')\,|^2 = \textstyle\sum_{m,m'} |\, x(n,\sigma_k,\sigma,j,m\,;\quad n',\sigma_k',\sigma',j',m')\,|^2 \\ +|\, y(n,\sigma_k,\sigma,j,m\,;\, n',\sigma_k',\sigma',j',m')\,|^2 \\ +|\, z(n,\sigma_k,\sigma,j,m\,;\, n',\sigma_k',\sigma',j',m')\,|^2,\end{aligned} \tag{1}$$

from which their explicit values are found to be:

$$\begin{aligned}|q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k\pm 1,\ \sigma\pm 1,\ j+1)\,|^2 &= D^2[O(j+1,\pm\sigma+1)/4(j+1)] \\ |\, q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k\pm 1,\ \sigma\pm 1,\ j)\,|^2 &= D^2[P(j,\pm\sigma)(2j+1)/4j(j+1)] \\ |\, q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k,\sigma,j+1)\,|^2 &= D^2[Q(j+1,\sigma)/(j+1)] \\ |q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k,\sigma,j)\,|^2 &= D^2[Q(\sigma,0)(2j+1)/j(j+1)],\end{aligned} \tag{2}$$

where:

$$\begin{aligned}O(a,b) &= (a+b)(a+b-1), & P(a,b) &= (a+b+1)(a-b), \\ Q(a,b) &= a^2-b^2, & D &= |\, D(n\,;\, n')\,|.\end{aligned} \tag{3}$$

In the usual treatment of the "symmetrical top," $\sigma=\sigma_k$; but it is to be noted again that here $\sigma=\sigma_k+\sigma_s$, where $\sigma_s=-s,\ -(s-1),\ \cdots,\ (s-1),\ s$. As $\Delta\sigma=\Delta\sigma_k$, we have $\Delta\sigma_s=0$—a selection principle which we have already quoted.

Amplitude matrices for case (b). These may be obtained by superposition of the London-Hönl[6] and Kronig-Russell-Sommerfeld-Hönl[12,13] intensity formulas. This procedure has, in fact, already been used by Mulliken,[14] who has given most of the intensity relations appropriate to case (b). The precession of $\mathfrak{d}_k$ around j_k in case (b) is analogous to that of $\mathfrak{d}$ around j in case (a), as $\mathfrak{d}_k$, $\mathfrak{d}$ are both directed parallel to the axis of figure, and therefore perpendicular to the angular momentum due to rotation of the nuclei about the center of gravity, with which $\mathfrak{d}_k$ and $\mathfrak{d}$ are compounded to form vectorially respectively in cases (b) and (a) the resultants j_k and j. Therefore if in case (b) we average over the various j values consistent with given j_k, and thereby expurgate the fine-structure caused by different orientations of the loosely-coupled vector $\mathbf{s}$, we must then have the same dependence on the quantum numbers σ_k, j_k as that on σ, j in case (a). This dependence is, of course, that furnished by the Hönl-London amplitudes already given. On the other hand the precession of j_k and $\mathbf{s}$ about their resultant j in case (b) is entirely analogous to that of $\boldsymbol{k}$ and $\mathbf{s}$ about j in the ordinary atomic "normal multiplets," for which the intensity formulas were proposed in-

[11] A quantity is said to be "Hermitian" if interchanging the first and second sets of indices changes the quantity into its conjugate; i.e., if $f(a;a')=f^*(a';a)$.

[12] A. Sommerfeld and H. Hönl, Sitzungsberichte der Preuss. Akad. der Wissenschaften IX, 141 (1925). R. de L. Kronig, Zeits. f. Physik **31**, 885 (1925).

[13] H. N. Russell, Nature **115**, 835 (1925).

[14] R. S. Mulliken, Phys. Rev. **30**, 138 (1927); **30**, 785 (1927).

dependently by Kronig,[11] Sommerfeld and Hönl,[12] and Russell,[13] and justified in quantum mechanics by Dirac.[15] Thus proper relative intensities for given j_k but variable j can be obtained simply by substituting j_k for k in the ordinary atomic formulas (or j_k, j, s, m for $K-\frac{1}{2}$, $J-\frac{1}{2}$, $R-\frac{1}{2}$, M in terms of the Landé notation employed by Kronig). The absolute values of the intensities are obtained by proper normalization of Kronig's constant factors of proportionality B which are independent of j, i.e., of the relative orientation of k and s. This normalization is effected by securing agreement with the Hönl-London formulas in the manner described at the beginning of the paragraph. This can be done by making the B-factors such functions of j_k and σ_k that Kronig's intensity formulas become identical with those of Hönl and London provided in the former we set $j=j_k$, $s=0$ and in the latter $\sigma=\sigma_k$. This assumes that B is independent of s, a supposition which is legitimate since the precessions arising from the spin surely cannot appreciably affect the total intensity of radiation.

The above procedure for superposing the Kronig and Hönl-London formulas is reminiscent of what Kemble called the "hypothesis of continuity of intensities" in the old quantum theory and may be given a more rigorous proof by means of the principle of spectroscopic stability which is one of the important consequences of the new quantum mechanics. Consider an external field strong enough to overpower the internal coupling between $\mathbf{j}_k$ and $\mathbf{s}$, so that the projection of each along the field is quantized separately, and let m_k and m_s be the corresponding magnetic quantum numbers. As the spin is then completely split off from the rest of the molecule, the coordinate matrices will be identical with those for case (a) except that j_k and σ_k will replace j and σ. The principle of spectroscopic stability shows that an expression such as

$$\sum_{m_k,m_s,m_k',m_s'} \left| q(n,\sigma_k,j_k,m_k,m_s;\, n',\sigma_k',j_k',m_k',m_s') \right|^2 \tag{4}$$

s invariant of the mode of quantization and hence must be equal to the expression

$$\sum_{j,m,j',m'} \left| q(n,\sigma_k,j_k,j,m;\, n',\sigma_k',j_k',j',m') \right|^2 \tag{5}$$

which represents the quantization for case (b) in the absence of strong external fields. Here t may be taken to be any function of the coordinate matrices, and in particular may be considered to represent the sum of the squares of the x, y, z coordinate elements in a fashion analogous to Eq. (1). Now in the case of the strong field $\Delta m_s=0$, and further the coordinate matrices are independent of m_s since the spin is not coupled to the rest of the molecule. Hence (4) becomes

$$(2s+1)(2j_k+1) \sum_{m_k'} \left| q(n,\sigma_k,j_k,m_k;\, n',\sigma_k',j_k',m_k') \right|^2 \tag{6}$$

inasmuch as the Burgers-Dorgelo sum rule shows that the sum over m_k' is independent of m_k, and for a given j_k there are $(2j_k+1)$ values of m_k and $(2s+1)$ of m_s. The sum-rule also shows that the sum over j' and m' in (5) has a value independent of both j and m, and hence (5) becomes

$$(2s+1)(2j_k+1) \sum_{j',m'} \left| q(n,\sigma_k,j_k,j,m;\, n,\sigma_k,j_k,j',m') \right|^2 \tag{7}$$

as for given j_k there are $\sum_{j=|j_k-s|,\ldots,j_k+s}(2j+1)$ or $(2j_k+1)\,(2s+1)$ pairs of values of j and m. On equating (6) and (7) we obtain precisely the scheme for normalizing the Kronig B-factor described above.

On performing this superposition of the Kronig and the London-Hönl formulas, the following values have been found for the coefficients:

[15] P. A. M. Dirac, Proc. Roy. Soc. **111A**, 281 (1926).

$$\begin{aligned}
B(n,\sigma_k,j_k\,;\,n'.\sigma_k\pm1,j_k+1)&=iD(n\,;\,n')\,[O(j_k+2,\pm\sigma_k)/16U(j_k+1)\,]^{1/2}\\
B(n,\sigma_k,j_k\,;\,n',\sigma_k\pm1,j_k)&=\mp iD(n\,;\,n')\,[P(j_k,\pm\sigma_k)/16V(j_k)\,]^{1/2}\\
B(n,\sigma_k,j_k\,;\,n',\sigma_k,j_k+1)&=D(n\,;\,n')\,[Q(j_k+1,\sigma_k)/4U(j_k+1)\,]^{1/2}\\
B(n,\sigma_k,j_k\,;\,n',\sigma_k,j_k)&=D(n\,;\,n')\,[Q(\sigma_k,0)/4V(\,j_k)\,]^{1/2}.
\end{aligned}\tag{8}$$

It should be noted that these B's given above are proportional to the square roots of the Kronig factors, i.e., are $B^{1/2}$ in his notation.

The elements of the coordinate matrices (which are Hermitian[11]) may then be written as:

$$\begin{aligned}
x(j_k,j,m;\,j_k+1,j+1,m\pm1)&=iB(j_k;\,j_k+1)\,[E(i+1,j_k)E(j+2,j_k)O(j+2,\pm m)/4U(j+1)\,]^{1/2}\\
z(j_k,j,m;\,j_k+1,j+1,m)&=B(j_k;\,j_k+1)\,[E(j+1,j_k)E(j+2,j_k)Q(j+1,m)/U(j)\,]^{1/2}\\
x(j_k,j,m;\,j_k+1,j,m\pm1)&=\mp iB(j_k;\,j_k+1)\,[E(j+1,j_k)F(j-1,j_k)P(j,\pm m)/4V(j)\,]^{1/2}\\
z(j_k,j,m;\,j_k+1,j,m)&=B(j_k;\,j_k+1)\,[E(j+1,j_k)F(j-1,j_k)Q(m,0)/V(j)\,]^{1/2}\\
x(j_k,j,m;\,j_k+1,j-1,m\pm1)&=iB(j_k;\,j_k+1)\,[F(j-1,j_k)F(j-2,j_k)O(j,\mp m)/4U(j)\,]^{1/2}\\
z(j_k,j,m;\,j_k+1,j-1,m)&=-B(j_k;\,j_k+1)[\,F(j-1,j_k)F(j-2,j_k)Q(j,m)/U(j)\,]^{1/2}\\
x(j_k,j,m;j_k,j+1,m\pm1)&=-iB(j_k;j_k)\,[E(j+1,j_k)F(j+1,j_k)O(j+2,\pm m)/4U(j+1)\,]^{1/2}\\
z(j_k,j,m;\,j_k,j+1,m)&=-B(j_k;\,j_k)\,[E(j+1,j_k)F(j+1,j_k)Q(j+1,m)/U(j+1)\,]^{1/2}\\
x(j_k,j,m;\,j_k,j,m\pm1)&=\mp iB(j_k;\,j_k)\,[G^2(j,j_k)P(j,\pm m)/4V(j)\,]^{1/2}\\
z(j_k,j,m;\,j_k,j,m)&=B(j_k;\,j_k)\,[G^2(j,j_k)Q(m,0)/V(j)\,]^{1/2},
\end{aligned}\tag{9}$$

where:

$$\begin{aligned}
&E(j\,;\,j_k)=(j+j_k)(\,j+j_k+1)-s(s+1),\quad F(j\,;j_k)=s(s+1)-(j-j_k)(j-j_k+1),\\
&G(j\,;\,j_k)=j(j+1)+j_k(j_k+1)-s(s+1),\qquad U(a)=a^2(2a-1)(2a+1),\\
&V(a)=a^2(a+1)^2.
\end{aligned}\tag{10}$$

The definitions of the functions O, P, and Q are given in Eqs. (3).

In (9) we have omitted writing in explicitly the indices n, σ_k; n', σ_k' in the elements, but to get the complete formulas one has only to use the proper B-factors from (8). The elements of the y matrix can be obtained from those for x by noting that $x(m;\,m\pm1)=\pm iy(m;\,m\pm1)$. The phases given above were determined by comparison with the classical Fourier expansions of the coordinates just as Kronig found a set of phases for case (a).[16]

2. Energy Levels and Intensities in the General Intermediate Case

The feature which characterizes the present calculation is that we start with case (b) and work back to case (a); i.e., we at first neglect the interaction between the spin and electronic orbital angular momenta, then set up the Hamiltonian function representing this interaction and use the technique of the new quantum mechanics to determine the "Eigenwerte" and amplitudes in the general case. An alternative method would be to start with case (a); i.e., at first neglect the interaction between the rotation and the non-secular part of the spin precessions, and then calculate the effect of the

[16] R. de L. Kronig, Zeits. f. Physik **45**, 458 (1927).

centrifugal torques on these precessions. This method will be considered in a later paper by one of us.

Hamiltonian function. The particular form of the perturbing Hamiltonian function which we take is the ordinary "cosine" expression; i.e.,

$$H_p = A(\mathfrak{d}_k \cdot \mathbf{s}) = A(\sigma_{kx}s_x + \sigma_{ky}s_y + \sigma_{kz}s_z). \tag{11}$$

It has been shown[17] that this is the form of perturbing function to be expected for the spin electron moving in a Coulomb field, and is the form which is ordinarily used for this type of calculation.[18,19]

For the determination of the matrix elements of H_p we shall employ a calculation borrowed from the classical mechanics, but which is legitimate also in the quantum mechanics as only quantities which commute with each other are involved. The calculation given here is similar to the one used by Heisenberg and Jordan[18] in their work on the Zeeman effect in atomic spectra. A more rigorous treatment can be obtained by adapting some of the formulas of Dirac.[20]

We first note that H_p can have elements concerned only with transitions for which $\Delta j_k = 0, \pm 1$, as the relative orientations of $\mathbf{s}$ and $\mathfrak{d}_k$ are not affected by the precessions about j and about the axis of the external field. Let $\boldsymbol{q}$ be any vector fixed in the molecule, denote by q_z its z-component, and by $\bar{q}_z$ the time average of q_z. The matrix $\bar{q}_z$ is then formed by keeping only the diagonal elements of q_z. In order to find $\bar{q}_z$ we first project $\boldsymbol{q}$ along and at right angles to j, and then project these components on the direction of the external field. The components of $\boldsymbol{q}$ perpendicular to j have projections on the axis of the field which vary with the time, due to the precession about j, and hence do not contribute to $\bar{q}_z$. The motion of j about the axis of the field is one of pure precession without nutation, so that the component of $\boldsymbol{q}$ along j has a projection on the field which is independent of the time.

[17] L. H. Thomas, Nature **117**, 514 (1926); Phil. Mag. **3**, 1 (1927). J. Frenkel, Zeits. f. Physik **37**, 243 (1926).

[18] Cf. for example, W. Heisenberg and P. Jordan, Zeits. f. Physik **37**, 263 (1926). E. C. Kemble, ref.[2]

[19] In order to take account of the interaction between $\mathbf{s}$ and the field developed by the rotation of the nuclei about the molecular center of gravity, we should have $H_p = A(\mathfrak{d}_k \cdot \mathbf{s}) + K(\mathfrak{k} \cdot \mathbf{s})$ where $\mathfrak{k}$ is the nuclear angular momentum, but as $\mathfrak{k} = j_k - \mathfrak{d}_k$, we have $H_p = K(j_k \cdot \mathbf{s}) + (A - K)(\mathfrak{d}_k \cdot \mathbf{s})$. The first term contributes only to the diagonal elements of (20), while the second term changes slightly the proportionality constant between $(\mathfrak{d}_k \cdot \mathbf{s})$ and H_p. Due to the large masses of the nuclei, however, K is very much smaller than A, so that we neglect these terms. This effect should lead to a very small separation of (b) terms which would be of importance only for S states; this has been discussed by Kemble, and by Mulliken who refers to it as "ρ-type doubling."

[20] P. A. M. Dirac, Proc. Roy. Soc. **111A**, 281 (1926). Our Eqs. (17) and (16) correspond respectively to Dirac's Eqs. (48) and (60), while our Eq. (12) is analogous to his Eq. (61) considering only the first term of the right-hand side. However, his quantity r is our $\mathfrak{d}_k^{\text{perp}}$, and as the latter has elements which are functions of j_k, we would not have, in Dirac's language, the commutative property of r with $\epsilon^{i\theta}$ and $\epsilon^{-i\theta}$, a condition used in the derivation of his Eq. (60). This discrepancy can be easily remedied, using his Eqs. (39) and (50), and the final results are in complete agreement with our calculations.

The elements of $\bar{q}_z$ are made up entirely of contributions from this source. Now the component of $\boldsymbol{q}$ along j is $(\boldsymbol{q}\cdot j)/|j|$, where $j/|j|$ is the unit vector in the direction of j; and similarly the projection of this component on the external field is $[(\boldsymbol{q}\cdot j)/|j|](m/|j|)$, where $m=j_z$. Consequently

$$\bar{q}_z=(\boldsymbol{q}\cdot j)m/|j|^2. \tag{12}$$

We now identify $\boldsymbol{q}$ with the vector matrix $\mathfrak{d}_k$. The procedure for obtaining the elements of σ_{kx}, σ_{ky}, and σ_{kz}, is very similar to that used in obtaining the amplitudes for case (b). We need concern ourselves only with elements for which $\Delta\sigma_k=0$, as $\mathfrak{d}_k$ has no components at right angles to itself, and then normalize these elements so that the component along the axis of symmetry of the molecule has the value $|\mathfrak{d}_k|=\sigma_k$, for this component is nothing but $\mathfrak{d}_k$ itself.[21] The elements of σ_{kx}, σ_{ky}, σ_{kz}, then resemble, in a very striking manner, those elements of x, y, and z respectively for which the transitions are of the type $\Delta\sigma_k=0$; the only difference being (apart from the difference in the normalizing factors just mentioned) that owing to the constancy of σ_k the elements of σ_{kx}, σ_{ky}, and σ_{kz}, are diagonal with respect to transitions in the quantum numbers represented by the letter n. Mathematically stated,

$$\sigma_{kz}(j_k,j,m\,;\,j_k',j',m)=(\sigma_k/D(n\,;\,n))z(n,\sigma_k,j_k,j,m\,;\,n,\sigma_k,j_k',j',m).$$

Consider a resolution of $\mathfrak{d}_k$ into two components, parallel and perpendicular to j_k, respectively. Let us designate them as $\mathfrak{d}_k^{(\mathrm{par})}$ and $\mathfrak{d}_k^{(\mathrm{perp})}$. This resolution amounts to considering separately the elements of σ_{kz} for which $\Delta j_k=0$, and for which $\Delta j_k=\pm 1$.

Applying Eq. (12) to $\mathfrak{d}_k^{(\mathrm{par})}$, we have

$$(\sigma_k^{(\mathrm{par})})_z(j_k,j,m\,;\,j_k,j,m)=[|\mathfrak{d}_k^{(\mathrm{par})}||j_k|^2/|j_k|+(\mathfrak{d}_k^{(\mathrm{par})}\cdot\mathbf{s})](m/|j|^2), \tag{13}$$

where we have introduced the relation $j=j_k+\mathbf{s}$.

From the matrix expressions for $\mathfrak{d}_k$ and j_k it can be shown that[22]

$$(|\mathfrak{d}_k^{(\mathrm{par})}|/|j_k|)=\sigma_k^2/j_k(j_k+1). \tag{14}$$

Hence, using Eqs. (9) and (14), Eq. (13) can be written:

$$\begin{aligned}H_p&(n,\sigma_k,j_k\,;\,n,\sigma_k,j_k) \qquad (15)\\ &=A(\sigma_k/D(n\,;\,n))(j(j+1)/m)z(n,\sigma_k,j_k,j,m\,;\,n,\sigma_k,j_k,j,m)-A\sigma_k^2\\ &=A\sigma_k(j(j+1)/m)[B(n,\sigma_k,j_k\,;n,\sigma_k,j_k)/D(n\,;\,n)][G^2(j,j_k)Q(m,0)/V(j)]^{1/2}-A\sigma_k^2.\end{aligned}$$

Applying Eq. (12) to $\mathfrak{d}_k^{(\mathrm{perp})}$ we have from Eq. (9), as $(\mathfrak{d}_k^{(\mathrm{perp})}.\ j_k)=0$,

$$\begin{aligned}H_p&(n,\sigma_k,j_k\,;\,n,\sigma_k,j_k+1)=A(\sigma_k/D(n\,;n))(j(j+1)/m)z(n,\sigma_k,j_k,j,m\,;n,\sigma_k,j_k+1,j,m)\\ &=A(\sigma_k/D(n\,;\,n))B(n,\sigma_k,j_k\,;n,\sigma_k,j_k+1)[E(j+1,j_k)F(j-1,j_k)]^{1/2}\\ &=(A\sigma_k/2)[\{(j_k+1)^2-\sigma_k^2\}/(j_k+1)^2(2j_k+1)(2j_k+3)]^{1/2}\\ &\times[\{(j+j_k+1)(j+j_k+2)-s(s+1)\}\{s(s+1)-(j-j_k)(j-j_k-1)\}]^{1/2}. \qquad (16)\end{aligned}$$

[21] As $\mathfrak{d}_k$ represents only the projection of the total electronic orbital angular momentum vector k on the axis of symmetry, its absolute value is given by σ_k and not by $[\sigma_k(\sigma_k+1)]^{1/2}$.

[22] This formula can be obtained by combining the relations $|\mathfrak{d}_k^{\mathrm{par}}|/|\mathfrak{d}_k|=[\sigma_k^2/j_k(j_k+1)]^{1/2}$ and $|\mathfrak{d}_k|/|j_k|=[\sigma_k^2/j_k(j_k+1)]^{1/2}$ the second of which follows from the expressions for $|\mathfrak{d}_k|$ and $|j_k|$, while the first is obtained by use of the elements of $\mathfrak{d}_k$.

Similarly, by substituting from Eqs. (3), (8), and (10), Eq. (15) becomes,

$$H_p(n,\sigma_k,j_k\ ;\ n,\sigma_k,j_k)=A\sigma_k^2[\{j(j+1)-j_k(j_k+1)-s(s+1)\}/2j_k(j_k+1)]. \quad (17)$$

Energy determinant. According to the perturbation theory of the new quantum mechanics, the solution of our problem in the general case is essentially equivalent to the solution of the set of linear equations[23]:

$$W(r\ ;r')S(r\ ;r')-\sum_l H(l\ ;r')S(r\ ;l)=0, \quad (18)$$

subject to the auxiliary conditions:

$$\sum_l S(r\ ;l)S^*(r'\ ;l)=\begin{cases}0 \text{ if } r'\neq r\\ 1 \text{ if } r'=r.\end{cases} \quad (19)$$

Here r, r', and l assume all values of j_k consistent with a given set of values for σ_k, j, and s; i.e., r, r', $l=|j-s|, \cdots, (j+s-1), (j+s)$.

The condition for the existence of solutions, other than zero, of Eqs. (18) is that W satisfy the determinantal equation:

$$0=\begin{vmatrix} H(j_{k1}\ ;j_{k1})-W & H(j_{k1}\ ;j_{k1}-1) & \cdots & \cdots \\ H(j_{k1}-1\ ;j_{k1}) & H(j_{k1}-1\ ;j_{k1}-1)-W & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & H(j_{k2}\ ;j_{k2})-W \end{vmatrix}. \quad (20)$$

The symbols j_{k1} and j_{k2} designate respectively the largest and smallest values of j_k compatible with a given set of values for j and s; i.e., $j_{k1}=j+s$, $j_{k2}=|j-s|$.

The Hamiltonian function (which is Hermitian[11]) appearing in the above determinant is that part of the complete Hamiltonian function which involves j_k, and thus includes, besides H_p, diagonal terms concerned with the nuclear rotational energy. Thus $H=H_r+H_p$, where H_r is the diagonal matrix,

$$H_r(n,\sigma_k,j_k\ ;\ n,\sigma_k,j_k)=[j_k(j_k+1)-\sigma_k^2](h^2/8\pi^2I). \quad (21)$$

The elements of H_p are those given by Eqs. (16) and (17).

The values of W which satisfy the above determinant give the energy levels for the complete transition stage from case (b) where $IA=0$, to case (a) where $1/IA=0$. The asymptotic energy formula valid for large values of A must, of course, be that for the symmetrical top, and is hence

$$W=A\sigma_k\sigma_s+[j(j+1)-\sigma^2+\overline{s^2}_{\text{perp}}](h^2/8\pi^2I)+\cdots, \quad (22)$$

although, because of algebraic difficulties, we have not succeeded in showing that Eq. (22) follows from Eq. (20) except in special cases; e.g., doublets, and triplets. The first term arises from the interaction of $\mathbf{\sigma}_k$ and $\mathbf{s}$, while the second term represents the energy of molecular rotation. The term $(\overline{s^2}_{\text{perp}}\,h^2/8\pi^2I)$ must be included to take into account the fact that for case

[23] Born, Heisenberg, and Jordan, Zeits. f. Physik **35**, 557 (1926).

(a) the component of **s** perpendicular to the axis of figure makes a contribution to the energy.[24] In general $\overline{s^2}_{\text{perp}}=s(s+1)-\sigma_s^2$.

The energy determinant given above yields an algebraic equation for W of the same order as the term multiplicity $(2s+1)$, and so is not readily solvable except for low values of s, notably $s=\frac{1}{2}$, and $s=1$ (doublet and triplet spectra respectively). The results in these special cases will be given in later sections of this paper.

Energy formula for nearly case (b) *coupling with any multiplicity.* Although the energy determinant may not be solvable for the general case of any multiplicity, the energy can be obtained as a power series development in a suitable parameter, by use of the perturbation theory formulas.[23] This expansion will be valid only when the coupling energy H_p is small compared to the rotational energy H_r; in other words, only when Hund's case (b) is a closer approximation than his case (a). Taking $\alpha=AI$ as the parameter for the expansion, the perturbing Hamiltonian function can be written as: $H=H_r+(H_p/AI)\alpha$, and the perturbation theory formulae[23] show that

$$W=H_r(j_k\,;j_k)+(1/AI)H_p(j_k\,;j_k)\alpha + (1/A^2I^2)\sum_{j_k'\neq j_k}[\,|\,H_p(j_k\,;j_k')\,|\,^2/h\nu_0(j_k\,;j_k')]\alpha^2+\cdots. \quad (23)$$

where

$$h\nu_0(j_k\,;j_k')=[j_k(j_k+1)-j_k'(j_k'+1)](h^2/8\pi^2I)\,; \quad (24)$$

and where the elements of H_r and H_p are given by Eqs. (16), (17), and (21).

Intensity relations. In case the energy determinant (20) can be solved, the "Eigenwerte" are to be substituted in Eqs. (18) and the elements of S determined. If q_b is any one of the coordinate matrices for case (b) and if q is the corresponding matrix in the general case, then[23]

$$q=Sq_b\tilde{S}^*, \quad (25)$$

where $\tilde{S}^*$ is the matrix formed from S by taking the conjugate of every element and then transposing the rows and columns (indicated by $\sim$).

Energy levels in the triplet case for coupling nearly of type (a). Here and throughout the remainder of this paper we shall use the abbreviation

[24] Born and Oppenheimer, Annalen der Physik, **84**, 457 (1927), especially p. 479. The term $\overline{s_{\text{perp}}^2}$ is theoretically just as important and inevitable as the other additive term $-\sigma^2$, but, unlike the latter, seems usually to be omitted by the band spectroscopists. It is particularly important to include this term if one is endeavoring to calculate the part of a multiplet which is due to magnetic coupling independent of a rotation, but fortunately in the particularly common case of doublets $\overline{s_{\text{perp}}^2}$ has the same value 1/2 in both the components $\sigma_s=-1/2$ and $\sigma_s=1/2$. Instead of $\overline{s_{\text{perp}}^2}$ we ought really to write $\overline{(k+s)_{\text{perp}}^2}$ in order to include the secular effect of both the orbital and electronic angular momentum. However, the average value of $\mathbf{s}_{\text{perp}}\cdot\mathbf{k}_{\text{perp}}$ is zero, as $\mathbf{k}$ precesses very much faster than **s**, and further the mean square of the perpendicular component of $\mathbf{k}$ has the same value for all the components of a multiplet, and so for our purposes it does no harm to consider the secular effect of only the spin angular momentum perpendicular to the axis of figure. As the motion of **s** is very approximately that of pure precession without appreciable nutation it is not really necessary to affix a mean value sign above the square of the perpendicular component of **s**.

$$\lambda = 8\pi^2 AI/h^2. \tag{26}$$

The value of λ is then a measure of the tightness of the coupling; i.e., it is very small for coupling nearly of type (b), and is large for nearly type (a). For triplet terms $s=1$, $2s+1=3$, and the energy equation (20) is a cubic; i.e.,

$$\begin{aligned}(W+A\sigma_k^2\lambda^{-1})^3 &- A\lambda^{-1}(3j^2+3j+2)(W+A\sigma_k^2\lambda^{-1})^2 \\ &+A^2\lambda^{-2}[-\sigma_k^2\lambda^2+4\sigma_k^2\lambda+3j^2(j+1)^2](W+A\sigma_k^2\lambda^{-1}) \\ &+A^3\lambda^{-3}[\sigma_k^2\lambda^2(j^2+j+2)-4\sigma_k^2\lambda(j^2+j+1)-j^2(j+1)^2(j-1)(j+2)]=0\end{aligned}$$

It has not been found possible to solve this equation generally, but asymptotic solutions can be obtained for the limiting cases (a) and (b). For (a) we expand W as a power series in λ^{-1} and solve for the coefficients by substitution in the above formula. There are three roots corresponding to the three values of σ_s; i.e.,

$$\begin{aligned}\sigma_s=+1) \quad & W = A\sigma_k+[j(j+1)-\sigma_k^2-2\sigma_k](h^2/8\pi^2I) \\ & \qquad +2A\sigma_k^{-1}\lambda^{-2}[j(j+1)-\sigma_k(\sigma_k+1)]+\cdots. \\ \sigma_s=0) \quad & W = [j(j+1)-\sigma_k^2+2](h^2/8\pi^2I)+4A\lambda^{-2}+\cdots \\ \sigma_s=-1) \quad & W = -A\sigma_k+[j(j+1)-\sigma_k^2+2\sigma_k](h^2/8\pi^2I) \\ & \qquad -2A\sigma_k^{-1}\lambda^{-2}[j(j+1)-\sigma_k(\sigma_k-1)]+\cdots.\end{aligned}$$

These expressions agree with the asymptotic formula (22). The expansion about case (b) can be made by using (23) and (24).

3. Doublet Case

Energy formula. For doublet spectra $s=\frac{1}{2}$, and the term multiplicity $2s+1=2$. In the limit of case (b) there are two values of j_k; namely, $j_1=j+\frac{1}{2}$, and $j_2=j-\frac{1}{2}$, so that the energy determinant (20) becomes:

$$\begin{vmatrix} A\lambda^{-1}[(j+\frac{1}{2})(j+\frac{3}{2})-\sigma_k^2]-A\sigma_k^2(2j+1)^{-1}-W & A\sigma_k[\{(j+\frac{1}{2})^2-\sigma_k^2\}^{1/2}(2j+1)^{-1}] \\ A\sigma_k[\{(j+\frac{1}{2})^2-\sigma_k^2\}^{1/2}(2j+1)^{-1}] & A\lambda^{-1}[(j^2-\frac{1}{4})-\sigma_k^2]+A\sigma_k^2(2j+1)^{-1}-W \end{vmatrix} =0$$

which has the solution

$$W=[(j+\tfrac{1}{2})^2-\sigma_k^2\pm\tfrac{1}{2}\{4(j+\tfrac{1}{2})^2+\lambda(\lambda-4)\sigma_k^2\}^{1/2}](h^2/8\pi^2I) \tag{27}$$

The upper sign corresponds to the state of higher rotational energy; i.e., to $j_1=j+\frac{1}{2}$.

This remarkably compact and convenient formula was originally given in a preliminary report on this work.[25] It is very gratifying that the new quantum mechanics yields such a simple expression where the old quantum theory gave only a series approximation; especially since this formula gives the energy values both for regular multiplets ($A>0$), and for inverted multiplets ($A<0$) throughout the entire range from (a) to (b).

[25] J. H. Van Vleck and E. L. Hill, Phys. Rev. **31**, 714 (1928). Abstract. Our previous definition of the coupling factor A differs from the present one by $4\pi^2/h^2$, as we now measure angular momentum in multiples of $h/2\pi$.

Correlation of term values between (a) and (b). One of the most interesting properties of our doublet formula is that it yields in an unambiguous manner exactly that correlation of term values between (a) and (b) which has been predicted by Hund[26] and by Kemble.[2] In each of the limiting cases there are two component levels; i.e.,

case (b)	*case (a)*
$j_1=j+\frac{1}{2}$	$\sigma_1=\sigma_k+\frac{1}{2}$
$j_2=j-\frac{1}{2}$	$\sigma_2=\sigma_k-\frac{1}{2}$

The assignment of the two levels of case (b) to the two branches of (27) is known; namely, the level associated with the positive radical is the j_1 state. To find the assignment for case (a) consider an adiabatic change in the parameter λ from zero to a numerically large value. Whether λ be positive or negative, the discriminant of (27) never vanishes, except for the lowest state $j=\sigma_k-\frac{1}{2}$. Thus the two branches can be considered separately, and we have only to determine how each branch behaves during the change from (b) to (a). The lowest state must be investigated separately.

Regular multiplets $(A>O)$. Expanding (27) as a power series in the parameter $|\lambda^{-1}|$, we have

$$W=\pm\tfrac{1}{2}A\sigma_k+(h^2/8\pi^2I)\left[j(j+1)-(\sigma_k\pm\tfrac{1}{2})^2+\tfrac{1}{2}\pm\lambda^{-1}\sigma_k^{-1}\left\{(j+\tfrac{1}{2})^2-\sigma_k^2\right\}+\cdots\right]$$

The upper sign corresponds to the j_1 state for (b), and a comparison with the asymptotic formula (22) for (a) shows that it corresponds also to σ_1. Hence the correlation of energy levels is

$$j_1\rightarrow\sigma_1, \quad j_2\rightarrow\sigma_2. \tag{28}$$

For the lowest rotational state $j=\sigma_k-\frac{1}{2}$, the j_2 level does not exist, due to the restriction $j_k\geqq\sigma_k$, so that this state is a singlet. Eq. (27) becomes $W=(h^2/8\pi^2I)\left[(1-4\pi^2AI/h^2)\sigma_k\right]$. On comparison with (22) we see that $\sigma_s=-\frac{1}{2}$, so that for this state the behavior is anomalous (the radical changing sign) and the correlation is $j_1\rightarrow\sigma_2$, just as predicted by Hund and Kemble.

Inverted multiplets $(A<O)$. In this case (27) becomes:

$$W=\mp\tfrac{1}{2}A\sigma_k+(h^2/8\pi^2I)\left[j(j+1)-(\sigma_k\mp\tfrac{1}{2})^2+\tfrac{1}{2}\mp\lambda^{-1}\sigma_k^{-1}\left\{(j+\tfrac{1}{2})^2-\sigma_k^2\right\}+\cdots\right]$$

As for regular multiplets, the upper sign is correlated with the j_1 level for (b), but comparison with (22) shows that it is correlated with the σ_2 level for (a). Thus the term correlation is just the reverse of that for regular multiplets; i.e.,

$$j_1\rightarrow\sigma_2, \quad j_2\rightarrow\sigma_1. \tag{29}$$

As the discriminant of (27) never vanishes for negative values of A, there is no anomalous behavior for any of the rotational states.

[26] F. Hund, Zeits. f. Physik **42**, 93 (1927). Cf. especially his Fig. 8.

Doublet states for OH λ2811. This is the band used by Kemble[2] to test his formulas, and we shall take the necessary numerical data from his paper. As (27) gives the combined effects of rotational and spin energy in a given state, the energy difference between two doublet levels due to spin effects alone cannot be separated out, but it will be sufficient for our purposes to consider only the excess energy of each level over that which it would have were it a pure case (b) state having rotational energy only. With this simplification we readily find from (27) that the doublet energy difference is

$$\Delta=(h/8\pi^2cI)\left[\left\{4(j+\tfrac{1}{2})^2+\lambda(\lambda-4)\sigma_k^2\right\}^{1/2}-(2j+1)\right]\ \text{cm}^{-1}.$$

This particular band is due to a $^2S\rightarrow{}^2P$ transition; i.e., $\sigma_k=0\rightarrow\sigma_k=1$. For the ^2S state, as $\sigma_k=0$, the levels are singlets, while in the ^2P state they are doublets. This state is also inverted, so that $A<0$. According to the data given by Kemble in his Table II, the asymptotic value of the doublet separation at the origin is 140.25 cm^{-1}. The value of the constant $(h/8\pi^2cI)$ is obtained as the arithmetic average of B_1^* and B_2^*. Putting these numerical values into the above formula, it becomes,

$$\Delta=37.16\left[\left\{(j+\tfrac{1}{2})^2+21.79\right\}^{1/2}-(j+\tfrac{1}{2})\right]\ \text{cm}^{-1}.$$

Taken as a function of j this formula gives a curve practically coincident with curve c of Fig. 4 of Kemble's paper, and hence still leaves a small discrepancy with the experimental data, which may be due to our neglect of ρ-type doubling as suggested by Kemble, and may also be partly due to the somewhat arbitrary meaning which we have assigned to Δ. On calculating the values of B_1^* and B_2^* which are the "apparent" values of the constant $(h/8\pi^2cI)$ in the two component levels, they turn out to be 16.697 cm^{-1} and 20.566 cm^{-1} respectively, as compared to the experimental values of 16.60 cm^{-1} and 20.565 cm^{-1}, whereas Kemble's formula gave 16.82 cm^{-1} and 20.86 cm^{-1}.

Intensity formulas. Putting the energy values from (27) into (18), we get

$$\begin{aligned} S(j_1\,;j_1)&=C_1[H(j_2\,;j_1)], & S(j_1\,;j_2)&=C_1[W(j_1)-H(j_1\,;j_1)]\\ S(j_2\,;j_1)&=C_2[H(j_2\,;j_1)], & S(j_2\,;j_2)&=C_2[W(j_2)-H(j_1\,;j_1)] \end{aligned} \tag{30}$$

where the constants C_1 and C_2 are to be determined by use of (19). We have here introduced specifically the notation j_1 and j_2 for the two values of j_k. We shall throughout the rest of the paper write the elements of S in this condensed notation in which we omit writing all arguments except the j_k, as S is a diagonal with respect to other quantum numbers. The C's may in general have arbitrary phase factors but it will be shown below in fine print that for our purposes they can be disregarded, so that we can take the elements of S to be real. If then we introduce the abbreviations:

$$\gamma_1=\left\{\lambda\sigma_k^2(2j+1)^{-1}\right\}-(j+\tfrac{1}{2}) \tag{31}$$

$$2\gamma_2=\left[(2j+1)^2+\lambda(\lambda-4)\sigma_k^2\right]^{1/2}, \tag{32}$$

and utilize the relation $\gamma_1^2-\gamma_2^2=[\sigma_k^4\lambda^2/(2j+1)^2]-(\sigma_k^2\lambda^2/4)$ we find that after the normalization (19) becomes

$$\begin{aligned} S(j_1\,;\,j_1)&=S(j_2\,;\,j_2)=[(\gamma_2-\gamma_1)/2\gamma_2]^{1/2}\\ S(j_1\,;\,j_2)&=-S(j_2\,;\,j_1)=[(\gamma_1+\gamma_2)/2\gamma_2]^{1/2}\end{aligned} \tag{33}$$

The intensity formulas for the general intermediate case can now be found by Eq. (25) and the expressions for S given in (33) and for q_b given in (9). We have verified directly in a large number of instances that in the limit $\lambda=\infty$ Eq. (25) actually converts the (b)-formulas (9) into the Hönl-London (a)-formulas. It is interesting to note that the selection rule $\Delta\sigma_s=0$ for case (a) can actually be established in this way, as we find the elements of the left side of (25) for which $\Delta\sigma_s\neq 0$ vanish in the limit $\lambda=\infty$.

As most readers are probably more familiar with the amplitudes for (a) than for (b) we shall give an alternative method, perhaps simpler than (25) for finding the general intensities, starting instead with those for case (a). This method has the further practical advantage that because of the selection rule $\Delta\sigma_s=0$ there are never more than two terms in the summations involved in expanding the matrix products, whereas with (25) there may be three or more terms in this summation. The idea is to transform from (a) to (b) and then from (b) to the general case. Thus if q_a, q_b, and q, represent any given coordinate matrix for case (a), case (b), and the intermediate case respectively, and if S_1 is the matrix $S_1=\lim_{A\to\infty}S$,[27] then $q_a=S_1q_b\tilde{S}_1$, and as also $\tilde{S}_1=S_1^{-1}$, then $q_b=\tilde{S}_1q_aS_1$. But as indicated in the preceding paragraph, $q=Sq_b\tilde{S}$, hence

$$q=Tq_a\tilde{T}, \tag{34}$$

where

$$T=S\tilde{S}_1, \qquad \tilde{T}=S_1\tilde{S}. \tag{35}$$

From (33) and (28), letting $A\to\infty$,

$$\begin{aligned} S_1(\sigma_1\,;\,\sigma_1)&=\quad S_1(\sigma_2\,;\,\sigma_2)=[\{(j+\tfrac{1}{2})-\sigma_k\}/(2j+1)]^{1/2}\\ S_1(\sigma_1\,;\,\sigma_2)&=-S_1(\sigma_2\,;\,\sigma_1)=[\{(j+\tfrac{1}{2})+\sigma_k\}/(2j+1)]^{1/2}\end{aligned} \tag{36}$$

where we use the notation σ_1 and σ_2 instead of the double indices (σ_k, σ_s). Putting the expressions from (33) and (36) in (35) we get for regular multiplets,[27]

$$T(\sigma_1;\sigma_1)=T(\sigma_2;\sigma_2)=K[(\gamma_2-\gamma_1)(j+\tfrac{1}{2}-\sigma_k)]^{1/2}+K[(\gamma_1+\gamma_2)(j+\tfrac{1}{2}+\sigma_k)]^{1/2} \tag{37}$$

$$T(\sigma_1;\sigma_2)=-T(\sigma_2;\sigma_1)=K[(\gamma_1+\gamma_2)(j+\tfrac{1}{2}-\sigma_k)]^{1/2}-K[(\gamma_2-\gamma_1)(j+\tfrac{1}{2}+\sigma_k)]^{1/2} \tag{38}$$

where $\qquad K=[2\gamma_2(2j+1)]^{-1/2}.$

[27] In the remainder of this section we shall assume that $A>0$; i.e., the formulae are for regular multiplets, but they can easily be found for $A<0$ by defining $S_1=\lim_{A\to-\infty}S$. The form of the general equations (34) and (35) is, of course, unchanged.

These elements, of course, satisfy the conditions that $\lim_{A\to\infty} T=1$ and $\lim_{A\to 0} T=\tilde{S}_1$ (e.g., in the limit $A=\infty$, $T(\sigma_1;\sigma_1)=T(\sigma_2;\sigma_2)=1$; $T(\sigma_1;\sigma_2)=T(\sigma_2;\sigma_1)=0$). The explicit expansion for (34) is

$$q(n,\sigma_k,\sigma,j,m\,;\,n',\sigma_k',\sigma',j',m')=\sum_{\sigma'',\sigma'''}[T(n,\sigma_k,\sigma,j,m\,;\,n,\sigma_k,\sigma'',j,m)$$
$$\times q_a(n,\sigma_k,\sigma'',j,m\,;\,n',\sigma_k',\sigma''',j',m')T(n',\sigma_k',\sigma',j',m'\,;\,n',\sigma_k',\sigma''',j',m')], \quad (39)$$

where the q_a's can be taken directly from (2), and the T's from (37-8).

The summation over σ'' embraces only the two values $\sigma''=\sigma_k-\frac{1}{2}$, $\sigma_k+\frac{1}{2}$, and σ''' can only equal $\sigma''+(\sigma_k'-\sigma_k)$ since $\Delta\sigma_s=0$ in case (a). Consequently (39) *never involves a summation over more than two terms, and permits calculation of the intensity for any coupling intermediate between* (a) *and* (b) *in either the initial or final state or both.*

In the application of (39) to the calculation of intensities for particular transitions for which there are jumps in the electronic quantum numbers, it must be noted that although T is diagonal with respect to the quantum numbers represented by n, the elements of T still are functions of them through the coupling constant A and the moment of inertia I, which may be different for the upper and lower states. Consequently *in "electronic" bands the function T in front of q_a in* (39) *is of a different form (viz. has different constants I and λ) than the T after q_a.* Examples are given in section 4.

Question of phases. In using Eq. (25) to determine even only the magnitudes of the elements of q, it is essential that one know the phases as well as absolute values of the amplitudes q_b. For this reason we have in Eq. (9) given the amplitudes in case (b) inclusive of the phases. The phases of the final amplitudes q depend on how one choose the phases in the normalizing factors C_1 and C_2 involved in S (cf. Eq. 30). However, if, as is usually the case, we are interested in finding only the magnitudes of the elements of q by means of (25) the arbitrariness of phase in C_1 and C_2 is trivial. This is true because the C's are connected with only the first index in $S(j_k,j_k')$ or the last in the transposed matrix $S(j_k',j_k)$ and so the phase element coming from the C's is not involved in the variable or inner indices over which one sums in multiplying together the matrices involved in (25); thus the phase element of C merely introduces a complex factor of modulus unity into (25).

On the other hand at first sight it looks as though the phase of C might be of importance in using (34), for the phase of C is connected with the inner as well as outer indices in (34), as (35) shows that the construction of T involves transposition of S. In general one might expect that to use (34) correctly it is imperative to determine the phases in the C's in a way which is consistent with the phases in q_a; or in other words that (34) will work only with proper phases in the q_a. Now very fortunately there is the selection principle $\Delta\sigma_s=0$ in case (a) and consequently the differences between the initial and final quantum numbers in the elements q_a will be the same in both terms of the summation in (39). Further the phase factor depends on the difference of the quantum numbers; this can, for instance, be seen from the correspondence principle, as the difference of quantum numbers determines the corresponding classical harmonic. This means that the phase factor for q_a has the same values for both terms of the summation in (39), and so need not be included if we are interested in knowing the absolute values of the elements of q. Consequently we may take S to be real and need not consider the phases in the q_a (an advantage of 34 over 25). (One might perhaps question whether with the most general complex solutions of Schroedinger's equation the phase factors in q_a are functions only of the differences of the quantum numbers, but it is easily seen that if the phases in q_a were chosen in some more complicated way then with any simple choice of the phases in T, especially real T, that Eq. (34) would in the limit $A=0$ yield expressions for the elements of

q_b which are complex quantities neither real nor pure imaginaries, contrary to our selection of phases in the q_b in Eq. (9). In other words our choice of phases in the original unperturbed b-type system demands that the phases in q_a be functions only of the differences of quantum numbers).

4. Application of Doublet Intensity Formulas to Particular Transitions

As illustrations of the use of Eq. (39) we shall calculate the intensities for two transitions: i.e., (1) The important case of $^2P \rightarrow {}^2S$ in which ordinarily the ^2P state is case (a) and the ^2S state is case (b), and (2) a particular case of $^2D \rightarrow {}^2P$ in which ^2D is case (b) and ^2P is case (a). For both transitions we shall use unprimed letters for the quantum numbers in the upper state and primed ($'$) letters for those in the lower state.

$^2P \rightarrow {}^2S$. Eq. (38) shows that for the upper state $T=1$, while for the lower state $T=\tilde{S}_1$. Hence $q=1q_aS_1$, where

$$S_1(j_1' ; j_1') = S_1(j_2' ; j_2') = S_1(j_1' ; j_2') = -S_1(j_2' ; j_1') = (\tfrac{1}{2})^{1/2}.$$

The transitions involved may be conveniently divided, in the usual manner, into three groups for which $\Delta j = 0, \pm 1$, corresponding to the Q, P, and R branches respectively. Putting these values into (39) it is found that in any given branch the transition probabilities from a given level in the upper state to each of the levels $j_k' = j' \pm \frac{1}{2}$ in the lower state are equal. The following table gives the intensities for transitions from the two upper levels for each branch:

P-branch $\quad j' = j+1$; j_k' either $j'+\frac{1}{2}$ or $j'-\frac{1}{2}$.

$\sigma_1 \sim D^2[(4j^2-1)/32(j+1)]$; $\quad \sigma_2 \sim D^2[(2j+1)(2j+3)/32(j+1)]$

Q-branch $\quad j' = j$; $\quad j_k' = j' \pm \frac{1}{2}$

$\sigma_1 \sim D^2[(4j^2-1)(2j+3)/32j(j+1)]$; $\quad \sigma_2 \sim D^2[(2j+1)^3/32j(j+1)]$

R-branch $\quad j' = j-1$; $\quad j_k' = j' \pm \frac{1}{2}$

$\sigma_1 \sim D^2[(2j+1)(2j+3)/32j]$; $\quad \sigma_2 \sim D^2[(4j^2-1)/32j]$.

An interesting though qualitative correlation of these formulae with the experimental results can be made for the compounds HgH, ZnH, OH, and CH.[28] For HgH the ^2P level is, to a good approximation, case (a). There are twelve strong branches of which those differing only with respect to the final value of j_k' are of about equal intensities. This agrees very well with our conclusions concerning the equality in the intensities of transitions from a given σ-level in ^2P to either j_k-level in ^2S. In ZnH the ^2P level is not as near true case (a) as in HgH, and here the branches for which $\Delta j_k \neq \Delta j$ (i.e., $\Delta \sigma_s \neq 0$) are weaker than those for which $\Delta j_k = \Delta j$. In OH the weaker bands are reduced to satellite series and in CH they are practically absent. Considering this progression as one in which the ^2P state changes from (a) in HgH to practically (b) in CH, there is a general agreement in the experi-

[28] The writers are indebted to Prof. R. S. Mulliken for the experimental material in this section. Cf. also, R. S. Mulliken, Phys. Rev. **31**, 310 (1928) and especially Sept. 1928.

mental and theoretical intensities, as (9) shows that for transitions between two case (b) states the branches for which $\Delta j_k \neq \Delta j$ should be much weakened especially for the lines at some distance from the origin.

$^2D \rightarrow {}^2P$. For the upper state, which is taken as case (b)

$$T(j_1 ; j_1) = T(j_2 ; j_2) = [(j-\tfrac{3}{2})/(2j+1)]^{1/2}$$
$$T(j_1 ; j_2) = -T(j_2 ; j_1) = -[(j+\tfrac{5}{2})/(2j+1)]^{1/2},$$

while for the lower state $T=1$.

As the total intensities for the transitions from a given j_k-level in the upper state to each of the σ-levels in the lower state are here not equal, we give the expressions for all twelve branches.

P-branch $j'=j+1$

$j_1 \rightarrow \sigma_1 \sim D^2[(2j-1)(2j-3)^2/32(j+1)(2j+1)]$; $j_1 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j+5)/32(j+1)]$

$j_2 \rightarrow \sigma_1 \sim D^2[(2j-1)(2j-3)(2j+5)/32(j+1)(2j+1)]$; $j_2 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j-3)/32(j+1)]$

Q-branch $j'=j$

$j_1 \rightarrow \sigma_1 \sim D^2[(2j+5)(2j-3)^2/32j(j+1)]$; $j_1 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j+3)(2j+5)/32j(j+1)]$

$j_2 \rightarrow \sigma_1 \sim D^2[(2j-3)(2j+5)^2/32j(j+1)]$; $j_2 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j-3)(2j+3)/32j(j+1)]$

R-branch $j'=j-1$

$j_1 \rightarrow \sigma_1 \sim D^2[(2j-3)(2j+3)(2j+5)/32j(2j+1)]$ $j_1 \rightarrow \sigma_2 \sim D^2[(2j+3)(2j+5)/32j]$;

$j_2 \rightarrow \sigma_1 \sim D^2[(2j+3)(2j+5)^2/32j(2j+1)]$; $j_2 \rightarrow \sigma_2 \sim D^2[(2j-3)(2j+3)/32j]$.

5. Elementary Theory of σ-Type Doubling

A mathematical method very similar to that used in the preceding part of the paper may be used to demonstrate the existence of "σ-type doubling." Such doubling, as predicted by Hund[1] and Hulthén,[29] and as shown much more fully by Kronig,[30] arises because the molecular rotation removes the degeneracy caused by the identity of the energy for the states $-\sigma$ and $+\sigma$ in a stationary molecule. This hyper-doubling is not to be confused with the coarser spin doubling considered in sections 2–4, and the connection of the present section with the rest of the paper is in the type of mathematics rather than of doubling. The present treatment is not intended to include the interaction between spin and the σ-type degeneracy, and so applies primarily to singlet states. This interaction, which actually greatly influences the σ-doubling, will be considered in a later paper which will use case (a) as the unperturbed system and which will use a more complete perturbation theory better adapted to represent details of molecular structure than the simple "anschaulich" model used in this section. The characteristic feature of the present section is that even though we are calculating σ doubling primarily for case (a) we begin with Hund's case (d) as the unperturbed system. We, however, throughout simplify his case (d) by assuming no spin. Case (d) means that the electronic orbital angular momentum is so loosely coupled to the rest of the molecule that we no longer quantize its component in the direction of the axis of figure, just as in (b)

[29] E. Hulthén, Zeits. f. Physik, **46**, 349 (1927).

[30] R. de L. Kronig, Ibid., **46**, 814 (1928).

the spin s is no longer bound to this axis. We start calculating from (d) for two reasons: first, it is very easy to do this after the mathematics in the preceding sections, and second, even though a later paper will start with case (a) it is illuminating to calculate perturbations from both (a) and (d) and so pass continuously from one case to the other and vice versa.

The angular momentum vectors are the important factors in rotational distortions, and to represent their secular effect we may suppose the system to consist of two parts: (I) a "core" which is essentially the dumb-bell model of a diatomic molecule without electronic angular momentum and (II) an angular momentum vector $\boldsymbol{k}$ which represents at least qualitatively the angular momentum of the valence electrons. Let us suppose initially that the force field which part I exerts on part II is very nearly central. Then we have Hund's coupling (d) and the squares of the angular momenta of parts I and II are respectively $j_r(j_r+1)$ and $k(k+1)$, while the square of their resultant is $j(j+1)$. We use the notation j_r for the angular momentum of the core stripped of all electronic angular momentum, whereas the number j_k in case (b) included both nuclear and electronic orbital moments of momentum. Now introduce a coupling proportional to the square of the cosine of the angle α between $\boldsymbol{k}$ and the axis of part I. This, of course, destroys the centralness of the field. When this coupling is very tight, the square of the component σ[31] of $\boldsymbol{k}$ in the direction of this axis will have the quantized values $0, 1^2, 2^2, 3^2, \cdots$. Each of these values correspond to a pair of states, because of the possibility that σ be either positive or negative, or, more generally that the wave functions be two independent linear combinations of those for $-\sigma$ and $+\sigma$.[32] With a stationary molecule each constituent of a pair has the same energy $A\sigma^2$, where A is a proportionality factor determining the strength of the coupling introduced above, and our problem is to show that the Coriolis and centrifugal forces due to molecular rotation causes a small splitting of the energies associated with the two members of a pair. The mathematics for doing this is virtually identical with that used in section 2, except that now $\boldsymbol{k}$ rather than $\mathbf{s}$ is being bound to the axis of the molecule and that now the coupling energy is taken proportional to $\cos^2\alpha$ rather than $\cos\alpha$. The latter modification is, of course, to give equality of coupling energies between parallel and antiparallel positions and hence the degeneracy of the character associated with σ-type doubling. The matrix elements of $\cos\alpha$ may be obtained from those of $\cos(\sigma_k,s)$ given except for a factor $[A^2\sigma^2 s(s+1)]^{-1/2}$ in Eqs. (16–17) by substituting $\boldsymbol{k}$ for $\mathbf{s}$, j_r for j_k, and also setting $\sigma_k=0$ as the core is without electronic angular momentum. By the rules for matrix multiplication the elements of the coupling energy $Ak(k+1)\cos^2\alpha$ are then

[31] As we are not considering the spin, we may use the notation σ in place of σ_k.

[32] The values $-\sigma$ and $+\sigma$ correspond to factors in the wave function of respectively the form $e^{-i\sigma\phi}$ and $e^{+i\sigma\phi}$, where ϕ is an ignorable coordinate associated with rotation of the electrons about the axis of figure. However, the wave functions which remove properly the degeneracy in the problem of σ-type doubling turn out to have factors of the form $\cos\sigma\phi$ and $\sin\sigma\phi$, or are thus symmetrical and antisymmetrical combinations of the wave functions for the states $-\sigma$ and $+\sigma$. The writers are indebted to Professor Kemble for first calling this to our attention.

$$H_p(j_r,j_r')=0,\ j_r'\neq j_r,j_r\pm 2\ ; \qquad H_p(j_r\ ;j_r)=A\left[f(j_r)+f(j_r-1)\right]$$
$$H_p(j_r,j_r+2)=H_p(j_r+2,j_r)=A\left[f(j_r)f(j_r+1)\right]^{1/2} \tag{40}$$

with the abbreviation

$$f(j_r)=(j_r+k+j+2)(j_r+k-j+1)(j_r-k+j+1)(-j_r+k+j)/16(j_r+\tfrac{1}{2})(j_r+\tfrac{3}{2}).$$

The expressions H_p and f are functions of n, k, j as well as j_r, but for brevity we do not list n, j, k among the arguments as H is diagonal with respect to these quantum numbers. Precisely the same procedure as was used in deriving Eq. (20) shows that the energy levels W are the roots of the determinant

$$\left|\ H(j_r,j_r')-W\delta(j_r,j_r')\ \right|=0 \tag{41}$$

where the off-diagonal elements are identical with the expressions given in (40), while $H(j_r,j_r)$ equals $H_p(j_r,j_r)+Bj(j+1)$, as we must include the rotational energy of the core as well as the perturbing coupling energy. Here and elsewhere B is an abbreviation for the expression $h^2/8\pi^2I$ (not to be confused with the factor B used in section 1). The indices j_r and j_r' in (41) range from $j+k$ down to $j-k$ if $j>k$ or to $k-j$ if $j<k$. δ is the conventional symbol for an expression which equals unity when its arguments are equal and vanishes otherwise.

The determinant (41) yields an algebraic equation for W which can be solved exactly in the cases $k=\frac{1}{2}$, 1, $\frac{3}{2}$. This equation is respectively cubic and biquadratic for $k=1$ and $k=\frac{3}{2}$, but factors at once.[33] Half integral values such as $\frac{1}{2}$, $\frac{3}{2}$ for k are, of course, impossible if k represents real orbital angular momentum but nevertheless are of interest in showing the contraction of σ-type doubling with increasing σ. Also k could be half integral if it denoted the resultant of the orbital and spin angular momenta, provided they were so firmly coupled as to always form a quantized resultant (i.e., if Hund's interaction 3 is large compared to his 2 and 4; see p. 660 of ref. 1). This proviso is, however, an idealization seldom if ever met, as ordinarily in molecules the correction for the non-centralness of the field is much larger than the width of spin multiplets. The closed solutions for the cases $k=\frac{1}{2}$, 1, $\frac{3}{2}$ are as follows:

$$k=\frac{1}{2}, \qquad W=\frac{1}{4}A+B\left(j+\frac{1}{2}\right)\left(j+\frac{1}{2}\pm 1\right) \tag{42}$$

$$k=1 \quad \begin{cases} W=A+Bj(j+1) \\ W=\dfrac{1}{2}A+B(j^2+j+1)\pm\left[\dfrac{1}{4}A^2-AB+4\left(j+\dfrac{1}{2}\right)^2B^2\right]^{1/2} \end{cases}$$

$$k=\frac{3}{2} \quad \begin{cases} W=\dfrac{5}{4}A+B\left(j^2+\dfrac{3}{4}\right)\pm\left[A^2+(2j-3)AB+4j^2B^2\right]^{1/2} \\ W=\dfrac{5}{4}A+B\left(j^2+2j+\dfrac{7}{4}\right)\pm\left[A^2-(2j+5)AB+4\left(j+1\right)^2B^2\right]^{1/2} \end{cases}$$

[33] It is readily seen that for $k=3/2$ the first and third columns of the determinant in (41) must be proportional, also the second and fourth. Eq. (41) factors into two parts for any k, as by (40) the determinant in (41) involves no transitions between odd and even values of j_r.

For $A=0$ these formulas of course reduce to $Bj_r(j_r+1)$. Their significance for large A becomes more apparent if we develop the radicals as power series in the ratio[34] $1/\lambda=B/A$, which we may suppose small when the coupling is large and hence nearly type (a); and if in addition we group together the roots which correspond to the same values of k and σ. This is a different grouping than that on the basis of factorization given above. We then find

$$\left.\begin{aligned}
&k=\frac{1}{2},\ \sigma=\frac{1}{2}\Big) && W=\frac{1}{4}A+B\Big(j+\frac{1}{2}\Big)\Big(j+\frac{1}{2}\pm 1\Big). \\
&k=1,\ \ \sigma=0\ \Big) && W=0+B[j(j+1)+2]-4\lambda^{-1}Bj(j+1)+\cdots \\
&k=1,\ \ \sigma=1\ \Big) && W=A+Bj(j+1)+\lambda^{-1}B(2\pm 2)j(j+1)+\cdots \\
&k=\frac{3}{2},\ \sigma=\frac{1}{2}\Big) && W=\frac{1}{4}A+B\Big[j(j+1)+\frac{13}{4}\pm(2j+1)\Big]+\cdots \\
&k=\frac{3}{2},\ \sigma=\frac{3}{2}\Big) && W=\frac{9}{4}A+B\Big[j(j+1)-\frac{3}{4}\Big]+\frac{1}{2}\lambda^{-1}B\Big(3j^2+3j-\frac{9}{4}\Big) \\
& && \quad +\frac{3}{2}\lambda^{-2}B\Big[2\Big(j-\frac{1}{2}\Big)\Big(j+\frac{3}{2}\Big)\pm\Big(j-\frac{1}{2}\Big)\Big(j+\frac{1}{2}\Big)\Big(j+\frac{3}{2}\Big)\Big]
\end{aligned}\right. \tag{43}$$

Here and elsewhere we for brevity write σ for $|\sigma|$; it is impossible to specify the sign of σ as the Heisenberg resonance blends the states $-\sigma$ and $+\sigma$ (cf. note 32). The first term in the above formulas is, of course, the coupling energy $A\sigma^2$ for a stationary molecule, where σ is half integral rather than integral if k is also. The second term which is of the order B is in each case, except $\sigma=\frac{1}{2}$, equal to $B[j(j+1)-\sigma^2+(k^2+k-\sigma^2)]$, the familiar Kratzer-Kramers-Pauli expression as modified by Born and Oppenheimer[24] to include the secular effect of the component of electronic angular momentum which is perpendicular to the axis of figure in case (a), and whose square has the value $k_{\text{perp}}^2=k(k+1)-\sigma^2$ (cf. note 24). The remaining, higher order terms are ordinarily neglected, and are perturbations arising from the periodic part of this perpendicular component. A "σ-type doublet" is formed by energy levels corresponding to the plus and minus signs in (43) for given k and σ. The doublet width is, of course, proportional to the difference between the energy expressions evaluated with the plus and minus signs, and in each case the series development has been carried far enough to bring out this difference. The rotational distortion thus does indeed cause a splitting of the general type predicted by Hund. It is to be noted that the doublet width is in each cause of the order $B(1/\lambda)^{2\sigma-1}=A(1/\lambda)^{2\sigma}$, a result already mentioned in a footnote of Kronig's paper.[30] The variation of the doublet width with j is seen to be approximately as $j^{2\sigma}$ for large j; this, however, is without the spin, which modifies the situation considerably except in singlets. In the

[34] As we now have coupling proportional to the square rather than first power of the cosine, the constants A and λ have slightly different meanings than in sections 2–4 but we do not change the notation because their mathematical roles in series developments, etc., are virtually the same as before.

particular case $\sigma=\frac{1}{2}$, the doubling is of the same order B as the ordinary Kratzer rotational energy intervals, and so here the (a) type coupling always gives way to (d). In the case $\sigma=1$, the correction term of order $\lambda^{-1}B$, which gives the doubling, is proportional to $j(j+1)$, and so has the same effect as altering slightly the moment of inertia.

Correlation of values of j_r and σ. Although, barring $\sigma=\frac{1}{2}$, the levels coincide in pairs in the limit $\lambda=\infty$, members of such pairs pass adiabatically as the ratio $\lambda=A/B$ is gradually decreased, over into levels of distinctly different energy in the limit $A=0$. Using the same procedure as in the correlation given in Eqs. (28, 29) the adiabatic correlation is found by examination of the roots (41) to depend on the sign of A and to be as follows

$$A>0\begin{cases} k=1) & j_r=j-1\to\sigma=0\,; \qquad j_r=j,\ j+1\to\sigma=1 \\ & \text{except that when } j=0,\ j_r=1\to\sigma=0 \\ k=\frac{3}{2}) & j_r=j-\frac{1}{2},\ j-\frac{3}{2}\to\sigma=\frac{1}{2}\,; \qquad j_r=j+\frac{1}{2},\ j+\frac{3}{2}\to\sigma=\frac{3}{2} \\ & \text{except that when } j=\frac{1}{2},\ j_r=1,\ 2\to\sigma=\frac{1}{2} \end{cases}$$

$$A<0\begin{cases} k=1) & j_r=j+1\to\sigma=0\,; \qquad j_r=j,\ j-1\to\sigma=1 \\ k=\frac{3}{2}) & j_r=j+\frac{1}{2},\ j+\frac{3}{2}\to\sigma=\frac{1}{2}\,; \qquad j_r=j-\frac{1}{2},\ j-\frac{3}{2}\to\sigma=\frac{3}{2} \end{cases}$$

Combination relations. The correlation relations permit us to use formally the quantum number j_r instead of σ even in the limiting case (a). Let us call an energy level of type x or type y according as j_r+k is even or odd. Then in the limit $A=0$ (case d), the only possible transitions are those which join an x level and a y level; i.e., two x (or y) levels do not combine. This follows since in (d) the motion of the "core" (part I) and the motion of the valence electrons (part II) connected with the vector $\boldsymbol{k}$ are independent except that together j_r and $\boldsymbol{k}$ form the resultant $\boldsymbol{j}$. Hence in (d) a fixed electrical moment mounted along the axis of the core will obey the selection rules $\Delta j_r=\pm1$, $\Delta k=0$; the transition $\Delta j_r=0$ being absent since the core is non-gyroscopic, and jumps in k being absent because with no coupling the core does not experience any of the frequencies connected with the vector $\boldsymbol{k}$. Similarly in (d) an electrical moment associated with the motion of the valence electron will obey the rules $\Delta k=\pm1$, $\Delta j_r=0$; the former because the field which the core exerts on the valence angular momentum is assumed perfectly central in case (d), and the latter because of the absence of coupling with the axis of the core. Hence, regardless of whether we ascribe the electrical moment to the core or to the valence electrons, the elements of the moment q_d in case (d) are always of the form $\Delta(j_r+k)=\pm1$, and hence give only combinations between an x and a y level. Now when coupling is introduced, the moment in case (a), or in any case intermediate between (a)

and (d), is the matrix $q = Sq_dS^*$, where S is the transformation matrix whose elements are obtained by solving the system of linear equations connected with the determinant (41) (cf. Eq. (18)). Now the elements of S are all either of the form $x \rightarrow x$ or $y \rightarrow y$. This follows since the system of linear equations for determining S is separable into two independent systems involving only even or only odd values of j_r, inasmuch as the elements of the Hamiltonian function H are by (40) all of the form $H(j_r,j_r)$ and $H(j_r,j_r \pm 2)$. Combining the information which we have obtained about q_d and about S, and using the rules for matrix multiplication, we see that the only elements in q even in the general case are those which involve a transition from an x to a y level, or vice versa. Now the two members of a σ-type doublet are respectively x and y states, and further the x state is alternately the upper or lower level as j is successively increased by unity. This is verified directly up to $k = \frac{3}{2}$ by the correlation given above, and examination of the general behavior of the roots leaves little doubt but that this holds also for larger k values. We thus have the combination rules predicted empirically by Mulliken[35] and especially Hulthén[29] and explained by Kronig[30] from the symmetry properties of the Schroedinger wave function. We will not attempt to illustrate how these combination relations apply to transitions between particular types of spectral terms, as this is nicely covered by the diagrams in Hulthén's or Kronig's paper. Although Kronig neglected the perturbing effect of the component of electronic angular momentum perpendicular to the axis of figure in case (a), the present work shows that the combination relations hold even without this omission, and throughout the range from (a) to (d). Professor Kramers informs us that a similar result on the generality of the combination rules has been obtained by a different method in unpublished work of Wigner. We must emphasize that in deriving these relations we have made no effort to adequately take account of the spin, which will be considered in a later paper,[36] and conceivably the spin influence explains why combinations between two x or two y levels are apparently sometimes found experimentally.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MINNESOTA,
June 1, 1928.

[35] R. S. Mulliken, Phys. Rev. **28**, 1202 (1926).
[36] Abstract on p. 327 of this issue.

THE PROPAGATION OF SCHROEDINGER WAVES IN A UNIFORM FIELD OF FORCE

By G. Breit

Abstract

The phase-difference between a Schroedinger wave refracted by a uniform field of force and the primary wave is calculated. The results are shown in a table and graphically. As the wave-length increases, the phase-difference decreases, reaches a minimum, and then increases again. It is suggested that the intensity of some crystal reflections should vary anomalously as a result.

The motion of an electron in a uniform field of force has been treated by Kennard[1] from the point of view of the transformation theory and by Darwin[2] from the point of view of Schroedinger waves with particluar attention to Heisenberg's uncertainty principle. In these treatments, however, the simple problem of writing down a solution of Schroedinger's differential equation corresponding to a constant energy value has not been answered. This is done in the present note. Numerical values for the phase of the emerging wave are given. Relativity is neglected.

The electron having a charge e, mass m is moving in a uniform electric field of force directed along OY and having the absolute value F. The potential energy is Fy and the Schroedinger equation is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2mE}{h^2}\left(1-\frac{Fe}{E}y\right)\psi=0$$

or

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+k^2(1-ay)\psi=0 \tag{1}$$

where

$$k^2=8\pi^2mE/h^2, \qquad a=Fe/E \tag{2}$$

No generality is lost by confining our attention to waves having normals in the yx plane. Write

$$\psi=e^{i\xi x}f(y) \tag{3}$$

Then

$$d^2f/dy^2+(A-By)f=0 \tag{4}$$

where

$$A=k^2-\xi^2, \qquad B=k^2a \tag{5}$$

[1] Kennard, Zeits. f. Physik **44**, 326 (1927).

[2] Darwin, Proc. Roy. Soc. **A117**, 258 (1927).

Let $$\zeta = B^{-2/3}(A - By) \tag{6}$$

Then $$d^2f/d\zeta^2 + \zeta f = 0 \tag{7}$$

The general solution of this equation (7) is known to be

$$f = \zeta^{1/2} C_{1/3}(2\zeta^{3/2}/3) \tag{8}$$

where $C_{1/3}$ is the general cylindrical fuction of order 1/3.

Suppose the field of force F exists only for values of $y > 0$ and suppose it is required to find the phase of the reflected Schroedinger waves if they are incident from the side of $y < 0$. We must then satisfy the boundary conditions at the surface $y = 0$. For $y > 0$ we have a solution of the form (8). For $y < 0$ the solution consists of the sum of two waves, one being a plane incident and the other a plane reflected wave. We also must satisfy the condition that for $y = +\infty$ the expression (8) should give vanishing values of f.

Let the incident wave be represented by $\psi = a_i e^{i(\xi x + \eta y)}$ and the reflected by $a_r e^{i(\xi x - \eta y)}$. Then $\xi^2 + \eta^2 = k^2$. The refracted wave is of the form (8), i.e.

$$f = \zeta^{1/2}\{\alpha J_{1/3}(2\zeta^{3/2}/3) + \beta J_{-1/3}(2\zeta^{3/2}/3)\} = \alpha F(\zeta). \tag{9}$$

If the standard definitions of the J_n are used, namely, if the J_n are defined by their power series and continuations of these, it becomes clear on investigating the asymptotic expansions of the J_n that $\alpha = +\beta$. Thus we have the boundary conditions

$$a_i + a_r = \alpha F(\zeta_0) \quad \text{and} \quad i\eta(a_i - a_r) = \alpha (dF/d\zeta)_{\zeta_0} (d\zeta/dy)_{y=0} \tag{10}$$

Remembering (6) $(d\zeta/dy)_{y=0} = -B^{1/3}$. Using (5) $(d\zeta/dy)_{y=0} = -\eta/\zeta_0^{1/2}$ so that the second equation in (10) is

$$a_i - a_r = (i\alpha/\zeta_0^{1/2})(dF/d\zeta)_{\zeta_0} \tag{10'}$$

Combining this with the first equation in (10)

$$\frac{a_i - a_r}{a_i + a_r} = \frac{i}{\zeta_0^{1/2}} \left(\frac{d \log F}{d\zeta} \right)_{\zeta_0} = iK \tag{11}$$

Hence

$$a_i = \frac{1 + iK}{1 - iK} a_r \tag{12}$$

Since K is real, the amplitude of the reflected wave is therefore equal to that of the incident. Its phase, however, is different.

Using recurrence relations for Bessel fuctions, we find from (11) and (9)

$$K = \frac{J_{2/3} + J_{-2/3}}{J_{1/3} - J_{-1/3}} = \tan \epsilon \tag{13}$$

Here $\zeta_0 = AB^{-2/3}$ and so $2\zeta_0^{3/2}/3 = 2(k^2m^2)^{3/2}/3k^2a = 2km^3/3a = 4\pi m^3/3\lambda a$ where λ represents the wave-length for $y<0$. In the table below the values of K and ϵ are given as functions of the parameter

$$\kappa = 2\zeta_0^{3/2}/3 = 4\pi m^3/3\lambda a \tag{14}$$

Making use of Dinnik's tables[3] for $J_{1/3}$, $J_{-1/3}$, $J_{2/3}$, $J_{-2/3}$

TABLE I. *Values of K and ϵ for different values of κ.*

κ	K	$\tan^{-1}K$	2ϵ	κ	K	$\tan^{-1}K$	2ϵ
0.2	−1.91	−62.3°	−124.6	2.0	.337	18.7°	−322.6
0.4	−2.50	−68.1	−136.2	2.4	− .082	− 4.7	−369.4
0.6	−4.20	−76.4	−152.8	2.8	− .496	−26.3	−412.6
0.8	−21.8	−87.3	−174.6	3.2	−1.13	−48.5	−457.0
1.0	6.34	81	−198	3.6	−2.84	−70.5	−501.0
1.2	2.56	68.7	−223.6	4.0	18.1	86.9	−546.2
1.4	1.49	56.1	−247.8	4.4	2.04	63.9	−592.2
1.6	.939	43.1	−273.8	4.8	.820	39.3	−641.4
1.8	.589	30.5	−299.0	5.2	.288	16.1	−687.8

By (12) we have $a_i = e^{2i\epsilon}a_r$, the values of 2ϵ belonging to different κ being tabulated above. The phase of the reflected wave at $y=0$ is therefore retarded behind the phase of the incident wave by the amount $|2\epsilon|$. If $\kappa=0$, i.e., if the wave-length is large or if the incidence is glancing, the phase difference is 180°, as it should be because for long wave-lengths we deal

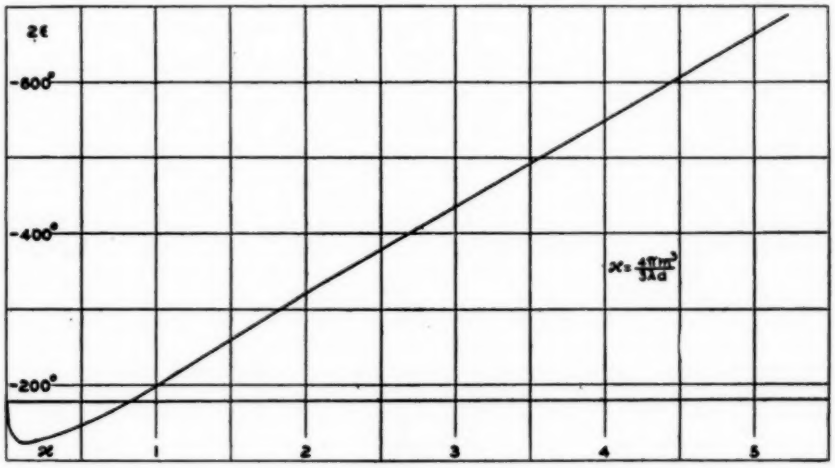


Fig. 1.

with pure reflection. If $\kappa>2$ we have approximately a linear dependence of 2ϵ on κ. This is the region where phase relations can be accurately described by refraction and using geometrical optics. It must be noted, however, that even for $\kappa>2$ an effect of the reflection is still felt in the form of

[3] Dinnik, Archiv d. Math. u. Phys. **18**, 337 (1911).

an additive constant of about 90° in the phase. This is particularly clearly seen on the attached graph, the asymptote to the phase curve cutting the axis of $\kappa=0$ at about 90°, while simple ray tracing leads to the expression

$$(-2\epsilon)=2\kappa \tag{15}$$

so that a change of 2π in 2ϵ should give a change of π in κ as is seen to be the case on the figure.

It seems possible that in the case of reflections of electrons by crystals the peculiar shape of the curve for $\kappa<2$ may be of importance. It is conceivable that α varies periodically over the surface of the crystal. The result of this would be a change in κ and therefore in 2ϵ. Hence the phase difference between the surface reflections from portions of the crystal having different values of a would be expected to vary with the wave-length and the angle of incidence. It is therefore to be expected that for electron reflections of the *plane grating type* a crystal cannot be described by a fixed distribution of reflecting matter as has been usually done in the case for x-rays.

DEPARTMENT OF TERRESTRIAL MAGNETISM,
CARNEGIE INSTITUTION OF WASHINGTON,
May 17, 1928.

THE CRITICAL POTENTIALS OF METALLIC VAPORS: I. COPPER

By H. B. Wahlin

Abstract

Using a method for determining the critical potentials of metallic vapors in which the metallic vapor is produced in the neighborhood of a gauze by vaporization of the gauze, it has been found possible to determine a number of critical potentials in Cu vapor in the region 0–20 volts. The values found in the region 0–11 volts, can be identified from the spectroscopically known energy levels. The interpretation of those above 11 volts is incomplete. Some of them agree with soft x-ray levels found by Thomas, and some with second ionization potentials determined by Russell. Whether the remaining levels correspond to spark terms or not remains to be seen.

Introduction

SINCE the amount of work being done on the organization and interpretation of the spectra of the metals has increased recently, a determination of the critical potentials of these elements becomes important as a check on the energy states of the atoms and the series limits of the spectra. Incidentally, such a determination will also serve as a check on recent theory of spectra.

Unfortunately the method of Franck and Hertz[1] and its modifications which yield such definite results in the case of those elements that can exist in the gaseous state at low temperatures cannot be used for those elements that require a high temperature for the production of the necessary vapor density. In the case of copper, for instance, a temperature of about 1300°C is required to produce a vapor pressure of 10^{-3} mm and at those temperatures insulation difficulties are such as to discourage experimentation.

It was in order to find a method which would remove some of these difficulties that the present work was undertaken. Obviously, if the metallic vapor and the heated portions of the tube containing the electrodes can be localized so that the leads to the outside can be kept cool and free from the deposits of metal, no difficulty with insulation should be experienced.

Experimental Arrangement

A modification of the three-electrode method was finally adopted. The chief difference lies in the fact that whereas in the method originally used the gas filled the whole tube, in the present scheme the gauze to which the electrons are accelerated is made of the metal under investigation, and this is heated by an electric current to such a temperature that vaporzation takes place. The maximum vapor density will then be in the neighborhood of the gauze, and the rest of the tube will be comparatively free from

[1] For a discussion of the methods used hitherto see Franck and Jordan's "Anregung von Quantensprüngen durch Stösse, Berlin (1926).

vapor. Electrons accelerated from the source to the gauze will at most make only a few impacts with atoms of the vapor before reaching the neighborhood of the gauze, and the energy loss due to momentum transfer will be slight. Thus the doubtful objection to critical potential determinations raised by some writers, viz., that the electrons do not reach the gauze with their full energy, is removed.

Fig. 1 shows the arrangement of electrodes used. S is an oxide-coated platinum plate which served as an equipotential source of electrons. This was heated from behind by the radiation from a flat tungsten spiral. D_1 is a diaphragm with a hole 5 mm in diameter, G is the gauze, D_2 is a second diaphragm, and R is the receiving electrode. These were enclosed in a Pyrex tube which was evacuated to a pressure between 10^{-5} and 10^{-6} mm. The gauze was heated by a direct current to the desired temperature. In order to keep the potential drop across the gauze as low as possible and thus prevent a change in the velocity distribution of the electron stream due to this drop, it was found advisable to work with gauzes of low resistance, and as a consequence, to use large currents for heating. In this work the potential drop across the gauze was about 0.5 volts and the drop across that portion directly opposite the hole in the diaphragm D_1 about 0.1 volt. The middle point of the gauze was connected to D_1, as shown in the diagram. The two were thus effectively at the same potential.

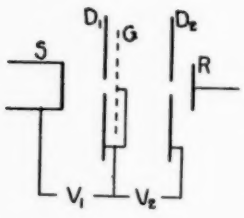


Fig. 1. Arrangement of electrodes.

The gauze was made by drilling holes in a piece of sheet copper 0.025-0.03 mm thick. With this thickness, a current of 15-20 amperes was sufficient to give a temperature of about 1050° which was found sufficient to produce the necessary vapor density. The temperature of the gauze was not uniform and portions of it may have been at a higher temperature.

Because of the magnetic field set up about the gauze, electrons accelerated from the source would not pass directly to the receiving plate, but would be deflected. It was necessary therefore to have the diaphragm D_2 slotted with the long axis of the slot perpendicular to the magnetic field.

A variable accelerating potential V_1 was applied between the source and D_1 and a constant accelerating potential of 2 volts between D_1 and D_2. A potential was also applied between D_2 and R to reduce the secondary emission from the receiving electrode. A shunted quadrant electrometer was used to measure the current. For currents such that a shunt resistance of 10^7 ohms or less was sufficiently high, "Glastor" grid leaks were found to be remarkably steady. When higher resistances were required, graphite marks on hard rubber were used.

The current was measured for various values of V_1 keeping V_2 fixed and the current-voltage curve plotted. The current was measured at 0.2 volt intervals between 1 and 20 volts.

Fig. 2 shows the types of curves obtained in the region 2-8 volts. Fig. 3 gives a magnified portion of another curve in the region 0-4 volts. Plotted to this scale, the breaks become somewhat more prominent. While the breaks are far from ideally sharp, they can still be determined with a good degree of accuracy when, as was the case here, the current is measured at equal voltage intervals. Then a change in slope corresponding to a break becomes noticeable through an increase in the difference between successive values of the current. The critical voltages can then be determined from the data directly, instead of from the curves. Since the current was measured at 0.2 volt intervals, the breaks could be accurately located within this range of voltage on any given curve.

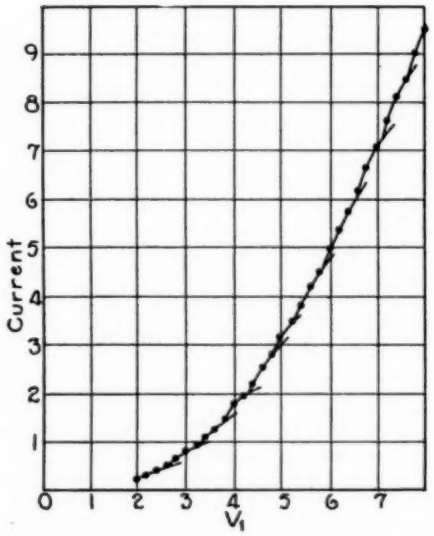


Fig. 2. Critical potential curve in the region 2 to 8 volts.

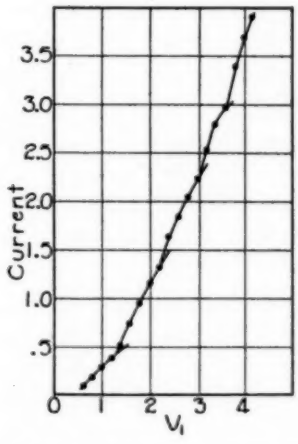


Fig. 3. Magnified portion of another curve.

In determining the critical potentials one break was taken as standard and assumed to be known, and the others determined in terms of this. This is equivalent to correcting for the contact e.m.f. between the oxide coated electron source and the gauze. This correction varied with the condition of the source, but in most cases was not more than 0.3 volt. The surprisingly low value of this correction may be due to metallic vapors depositing on the oxide plate and thus changing its nature.

Discussion of Method

In order to understand the shape of the critical potential curves, it will be well to consider the type of curve which might be expected under ideal conditions. Suppose that all the electrons emitted from the source had exactly the same velocity. With no vapor present a curve similar in shape to a current-voltage thermionic curve might be expected. If vapor were present

around the gauze but if no inelastic impacts occurred, some of the electrons would be scattered by impact with atoms of the vapor and would not pass through the opening in D_2. The result would thus be a general lowering of the curve. If, however, at a critical voltage, some of the electrons would make inelastic collisions with atoms of the vapor, these would, under the action of V_2, move toward the opening in D_2 and would become noticeable through an increase in the current to the receiving electrode. The effect would thus be a decrease in the scattered current due to the energy loss of some of the electrons. As the accelerating potential is increased, the electrons which suffer critical energy losses would retain some of their energy after impact, would again be scattered, and the current would decrease.

If instead of an isolated energy level, a gap, bounded on both sides by energy levels so close together that they could not be resolved by this method, were present in the energy level diagram, one would expect a decrease in the current as the energy of the electrons from the source exceeds the energy necessary to remove an electron from the lowest level of the atom to the level forming the lower boundary of the gap. When the voltage corresponding to the upper level is reached, there would again be an increase in the current.

Since the energy levels just below the level corresponding to ionization lie close together, it is to be expected that at the ionization potential an increase in the electron current without the preceding decrease would take place. This increase would be due chiefly to the electrons removed from the atoms.

These ideal conditions could not be approximated in the present experiments. The actual velocity distribution was such that the greater portion of the electrons had velocities extending over a range of about 1 volt. The effect of this would be, first, to make the breaks less sharp; and, secondly, to remove the decrease in the current following a critical potential. A reference to Figs. 2 and 3 shows that the experimental curves bear out these conclusions.

Three other factors besides inelastic collisions might enter into these experiments to influence the appearance and position of these breaks. First, it is well known in critical potential work that any change in the space charge around the gauze, such as would take place when the electrons lose their energy, will change the direction and magnitude of the electron stream; and, secondly, a selective scattering without loss of energy at a critical potential such as was first observed by Maxwell[2] and by Dymond[3] might produce an effect. The vapor available in most of the runs was so low that any change in space charge would probably not be noticeable. However, in order to determine definitely if these two factors have any influence, curves were taken with V_2 reversed and equal to 2 volts so as to retard the electrons. It was found that the breaks completely disappeared.

[2] L. R. Maxwell, Proc. Nat. Acad. Sci. **12**, 509 (1926).
[3] E. G. Dymond, Phys. Rev., **29**, 433 (1927).

This would not be the case if they were due to space charge or to selective scattering without energy loss.

The third factor which might play an important part is the emission of secondary electrons from the gauze or receiving electrode when bombarded by the primary beam. Farnsworth,[4] Petry,[5] and others have shown that there are definite critical changes in the magnitude of the secondary electron current from solids, when the velocity of the primary beam is changed. Any breaks which originate from these secondary electrons should persist if the gauze temperature were lowered. It was found that, if the temperature of the gauze was lowered so that no appreciable vaporization took place, the breaks completely disappeared.

It may be of interest to mention that if the critical potential curves were taken soon after the gauze had been introduced into the tube and before outgassing had progressed very far, that the breaks could be observed at a lower gauze temperature than when the outgassing was more nearly complete. An increased vaporization during outgassing, such as was first observed by Berliner,[6] would account for this. In addition to this increase in the vapor density, the increased gas pressure in the tube during outgassing would retard the diffusion of the vapor away from the gauze and would therefore act to increase the vapor density in the neighborhood of the gauze. Both these factors would increase the probability of the electrons making inelastic collisions and would enter into the explanation of the observed fact.

Discussion of Results

The spectrum of copper has been investigated by Shenstone,[7] Sommer,[8] and by Russell[9] and his co-workers. As will be seen from a comparison of the critical potentials calculated spectroscopically with the values obtained from these experiments (Table I), the agreement is quite close. The values given here differ slightly from those published in a preliminary notice which appeared in Nature,[10] but the difference is within the limits of experimental error.

These values are the average of from six to ten determinations. In no case is the maximum variation from the mean more than 0.2 volt, and in most cases less than that. The values enclosed in brackets are uncertain, because of possible overlapping of the error in the determination. Those marked "questionable" could only be repeated intermittently. A series of values were obtained between 2.1 and 2.6 volts which probably correspond to a group of critical potentials lying in this region. The variation was a

[4] H. E. Farnsworth, Phys. Rev. **20**,p. 358 (1922).
[5] R. L. Petry, Phys. Rev. **26**, 346 (1925).
[6] A. Berliner, Ann. der Physik **33**, 289(1888).
[7] A. G. Shenstone, Phil. Mag. **49**, 951 (1925).
[8] L. A. Sommer, Zeits. f. Physik **39**, 711 (1926).
[9] H. N. Russell, Astrophys. J. **64**, 184 and 233 (1927).
[10] H. B. Wahlin, Nature, p. 585, Oct. 22, 1927.

TABLE I. *Critical potentials in Cu and their interpretation.*

Critical potentials (volts)	Spectroscopic values	Transitions (Sommer)	Thomas' soft x-ray values	Russell's values (from spark)	Comment
1.38	1.38	$1^2S-{}^2D_3$			
2.0–2.6	2.13–2.39	${}^2D_{2,3}-2^2P_{1,2}$			
3.18	3.18	${}^2D_2-{}^4P_3$			questionable
3.73	3.77	$1^2S-2^2P_1$			
4.2	4.46	${}^2D_2-3^2P_1$			
4.8	4.87	$1^2S-{}^4P_3$			
5.67	5.75	$1^2S-{}^2D_3$			
6.09	6.09	$1^2S-3^2P_2$			
6.61	6.65 6.52	${}^2D_2-{}^2D_3{}^2$ 1^2S-3^2S			
7.06	7.10	${}^2D_2-{}^2G_4$			
7.72	7.69	$1^2S-\infty$			
8.14	8.28	$1^2S-{}^2D_3$			
8.71	8.73	$1^2S-{}^2G_4$			
9.0	8.95	${}^2D_2-\infty$			
9.42	9.27	$1^2S-{}^2P_1$			
9.98	10.01				
10.85	10.90	$1^2S-\infty$			
11.63					
12.4			12.3		quest onable
13.06					
14.0			14.2		
14.92					
15.52			15.7		
16.6					
17.16				17.1	
17.60				17.6	questionable
18.12					
18.60			19.0		
19.00					
19.68					

little too great to be ascribed to an experimental error in the determination of a single transition. These, together with the 3.18, 4.2, and the 7.06 values, are of interest since they could not be explained as due to transitions from the normal state of the atom. They agree reasonably well with transitions from the metastable ${}^2D$ state which serves as the ground level of the doublet-quartet series. In oder to have atoms in this state they would either have to be brought there by electron impact or else be vaporized in this state. A measurable positive ion current from the gauze was obtained even with $V_1=0$. If some of the Cu atoms come off positively charged, one might reasonably expect some of the atoms to be vaporized in the metastable ${}^2D$ state also. The number that would be produced in this way would probably be too small to be detectable. A study of these positive ion currents is being undertaken.

The alternative explanation of these transitions from the metastable state is that the atoms are brought into this state by electron impact. This means that in order to have transitions from this state, the atoms must have been struck twice by electrons. If this is the case, a decrease in the electron current should cause the breaks to disappear, since the probability of the transition would vary as the square of the current. It was necessary

to run the oxide source at a high temperature to prevent, as much as possible, the condensation of metallic vapors on it and thus changing the space current so that it was impossible to vary the current sufficiently to test this point with the present arrangement. It is hoped that further experiments will settle this question.

The critical potential at 9.42 volts may correspond to an ionization potential (the spectroscopic value given by Russell is 9.5 volts). The ionization potential at 10.85 volts agrees better with Russell's value (10.87 volts) than with Sommer's (10.90 volts), but the difference between these values is so small that it is impossible to determine from these experiments which is more nearly correct.

Our knowledge of higher critical potentials is still too scant to draw any definite conclusions about the values above 10.85 volts. The soft x-ray levels found by Thomas, together with the second ionization potentials given by Russell, have been listed for comparison. With a further knowledge of the spark term, it may be possible to determine to what the undesignated ones correspond.

While the method described above is far from ideal in that the breaks do not appear sharp on the curves, it has one important advantage over the three-electrode method as applied in earlier critical potential work, particularly in gases. In this work, V_2 was applied so as to retard the electrons coming through the gauze. Those electrons that made inelastic collisions were thus kept from reaching the receiving electrode. The effect on the current-V_1 curve was that at a critical potential there was a decrease in the current and a "hump" appeared in the curve. There has always been a question as to what points on successive humps should be taken for comparison. In the present method this difficulty does not enter, since the sharp increase in the current appears at the voltage where the inelastic collisions begin.

It is difficult to say just what range of metals can be covered by the present method. It seems likely, however, that for those metals that require a temperature of more than 1200 or 1300°C for the production of the necessary vapor density, radical changes will have to be made. At this temperature, thermionic emission from the gauze will become appreciable and may create a space charge around the gauze so as to alter the results.

A rather surprising thing is that the breaks appear as sharp as they do at the vapor densities available. The vapor pressure of copper at the melting point, and that was, of course, the limiting temperature that could be used in these experiments, is of the order of 10^{-4} mm, when the copper is thoroughly outgassed. At this pressure, the critical potentials should barely be noticeable. However, the good agreement of the values found with the ones calculated from spectroscopic data, together with the other evidence given earlier in this paper, leads to the conclusion that they originated in the vapor. The work is being extended to other metals.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WISCONSIN,
May 22, 1928.

NOTE ON THERMIONIC EMISSION

By Lewi Tonks

Abstract

Electron emission experiments can throw light on the surface heat of charging only if the density of electrons in equilibrium with an emitting surface is the same whether evaporation occurs with constant surface charge or with surface charge equal (and opposite in sign) to evaporated charge. This equality is proved thermodynamically in the present note.

IN A paper "On the Surface Heat of Charging"[1] it was pointed out that the difference between the cooling effect of electron emission ϕ_e and the work function determined from the temperature variation of the emission ϕ_e contains a term which is the surface heat of charging, P_s. This has been questioned[2] on the ground that the assumption in the original paper that ϕ_e is equal to ϕ_t, the thermodynamic work function, is wrong, and that the correct relation is

$$\phi_e = \phi_t - P_s$$

The argument is that under experimental conditions the electrons evaporate from a surface whose charge is constant. ϕ_t, however, is the voltage equivalent of the heat absorbed when electrons evaporate from an insulated emitter. Thus the heat absorption in the experimental case is $\phi_t - P_s$ and it is this quantity, not ϕ_t, which belongs in the exponent of the Richardson equation when that equation is applied to experimental results.

The object of the present note is to refute this argument by presenting a rigorous proof of the original assumption—namely, that the work function in the exponent of the Richardson equation is the same whether emission takes place at constant total charge (the usual theoretical case) or constant surface charge (the experimental case); that is, that $\phi_e = \phi_t$. This will substantiate the point of view put forward in the first paper.

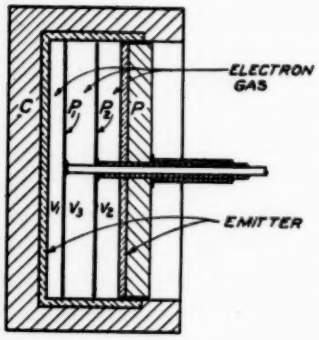


Fig. 1.

Suppose we have a cylinder and piston arrangement C, P (Fig. 1) having a large internal diameter, and throughout all operations with them let us keep the piston within a distance of the cylinder end which is very small compared with this diameter. The effect

[1] L. Tonks and I. Langmuir, Phys. Rev. **29**, 524 (1927).

[2] C. Davisson and L. H. Germer, Phys. Rev. **30**, 634 (1927). These authors also show that a term due to the energy of free electrons in the metal was neglected in the first paper. The present author wishes to acknowledge gratefully the clarification of his own ideas resulting from correspondence with Dr. Davisson.

of the sidewall of the cylinder upon the electric field and electron distribution in the enclosure can then be neglected, so that electric field, electron density, etc., are sensibly the same as for infinite plates. Let the inside of the cylinder and the end of the piston be completely covered with an electron emitter. The charge on the electrons results in a non-uniform density distribution in the enclosure, but even so, the application of thermodynamics to a volume-temperature cycle with this device leads to the Richardson equation.[3]

Now let us introduce a thin, movable, non-conducting, and perfectly reflecting partition P_1 between cylinder end and piston and parallel to them. It is obvious that the electron distribution and electric field remain unchanged. There is no force on P_1, for the electric fields and electron densities on its two faces are equal. Hence no work is done in moving it parallel to the cylinder axis, and no heat is absorbed by the system in so doing because every electron condensed on the advancing side of P_1 is balanced by one which evaporates on the receding side. The state of the electron gas after such a displacement is thus the same as before. Hence the motion of the partition can be made in an entirely arbitrary manner.

We can now use P_1 to prevent any change in the number of gaseous electrons in the volume V_1 when the piston is moved. In the case of ordinary evaporation this condition is fulfilled when P_1 is fixed. But with electrons the change in electric potential accompanying a motion of P causes a change in the average density of electrons in V_1, and to keep the total number constant, P_1 must move simultaneously with P. This can be accomplished by suitably gearing P_1 to P. A second partition P_2 may now be introduced between P_1 and P and it can be geared to P in such a way as to prevent evaporation or condensation from the piston. All evaporation is thus forced to take place at the small side-wall of the cylinder. This evaporation occurs at constant surface charge because the positive charge complementary to the evaporated electrons appears on cylinder end and piston.

It is almost obvious that the same final space distribution is reached after an expansion whether or not the partitions are present, that is, whether or not the evaporation of electrons takes place at constant surface charge. Were this not so, removal of the partitions (by sliding them out through slits in the cylinder walls, say) would leave the electron gas in a different state from that which would have been attained had the partitions never been introduced, and we should have the state of the gas dependent on its history.

How then is the unaltered distribution to be reconciled with the changed heat of vaporization? The answer is that thermodynamics deals with the total heat absorption of the system—not that at the surface of vaporization alone. Accordingly, to $\phi_t - P_s$, voltage equivalent of heat absorption on the side walls, must be added P_s, voltage equivalent of the heat absorbed in charging the cylinder end and piston positively. This gives ϕ_t as the voltage equivalent of the total heat absorption in this case just as in the usual

[3] C. Davisson, Phil. Mag. **47**, 544 (1924).

theoretical case in which the emitter hangs insulated in the middle of a piston-cylinder arrangement.

It is clear, then, that the exponential constant which is characteristic of the experimentally determined emission is ϕ_t, the result which was to be proved.[4]

It may be of interest to note that a question similar to the one answered here can arise in the case of ordinary vaporization. One recognized method of determining vapor pressure is to measure the loss of weight of the substance in a known time during which the material has been kept in a vacuum. Although the heat absorption for vaporization into a vacuum is $kT/2$ less than under equilibrium conditions, no corresponding differences in vapor pressure are either expected or found.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
May 8, 1928.

[4] It is assumed, of course, that the correction for the Schottky effect has been made.

THE COMBINATION OF HYDROGEN AND OXYGEN BY ELECTRIC DISCHARGES

By Rogers D. Rusk

Abstract

Combination of hydrogen and oxygen in the Geissler discharge, low-voltage arc and electrodeless discharge.—It was noted that combination ceased to be explosive in equivalent volumes of the two gases at pressures below 3 cm. Logarithmic decrease in pressure was obtained in equivalent volumes in the Geissler discharge for constant current, whereas excess oxygen increased and excess hydrogen decreased the rate of combination, a similar change in rate having been noted by Lind in his alpha-ray experiments.

Number of water molecules formed per pair of ions, as function of pressure.—From a consideration of the number of ions present in the Geissler discharge it appears that the number, k, of water molecules formed per pair of ions at the lower pressures is much less than unity, but that it increases with increasing pressure and may approach the value obtained by Lind at somewhat higher pressures. The pressure at which k approximates unity is such that the time between molecular collisions is of the order of magnitude of the life of an excited hydrogen atom. This is consistent with the view that combination may be due to some similar type of excitation produced by a process secondary to ionization.

THE combination of hydrogen and oxygen by alpha-ray impact was obtained and studied by S. C. Lind[1] in 1919. More recently, Dickinson[2] has obtained a slow but distinct combination in the presence of excited mercury vapor, and Mitchel[3] has studied the decrease in the rate of this combination caused by adding argon to the gaseous mixture. As is well known, the combination of hydrogen and oxygen by catalysis alone has been the subject of numerous investigations chief among which are those of Bone[4] and Langmuir.[5]

Lind concluded from his work that 3.9 molecules of water are formed per pair of ions, this value appearing to be fairly constant throughout a large pressure range down to 30 mm. At the lower pressures a somewhat greater rate is attributed to recoil atoms. Lind's result that 3.9 molecules of water are formed per pair of ions may be taken to indicate that the single ions themselves are not the ultimate combining units, but that they are the agents of a more complicated process.

Dickinson interprets his results as evidence of collisions of the "second kind" with consequent dissociation of the hydrogen and combination with the oxygen. Mitchel, whose work followed Dickinson's, noted an abnormal decrease in the rates of combination when argon was added, and he suggests

[1] Lind, Jour. Am. Chem. Soc. **41**, 531 (1919).
[2] Dickinson, Proc. Nat. Acad. Sci. **9**, 10, 409 (1923).
[3] Mitchel, Proc. Nat. Acad. Sci. **11**, 458 (1925).
[4] Bone, Trans. Far. Soc. **17**, 658 (1921–22).
[5] Langmuir, Trans. Far. Soc. **17**, 621 (1921–22).

the possibility that the active hydrogen is not atomic but molecular in some definite state of excitation. This suggestion implies that a part of the active hydrogen is deactivated by collision with the argon thereby abnormally reducing the rate of combination with the oxygen.

In the present experiment it was proposed to attempt the combination of hydrogen and oxygen in the Geissler discharge, low voltage arc and electrodeless discharge; and to measure and compare the rates of combination so obtained in order to throw light if possible upon the mechanism of combination. More than a hundred different sets of measurements were made with different proportions of hydrogen and oxygen. The preliminary data[6] previously reported upon were for total pressures of from 0.01 mm to 0.1 mm, but later measurements with Geissler discharges were extended to 5 mm pressure. The combination which was attempted by x-rays[6] appears to be inappreciable with the radiation from an old style Mueller tube when the experimental tube is carefully screened from stray charges.

Apparatus and Experimental Method

Preliminary experiments were made to determine the pressures at which the discharges could be obtained safely without fear of explosion. With a two to one ratio of hydrogen to oxygen, either an electric spark or hot filament caused explosion at pressures down to about 3 cm at which point the sudden explosion gradually became a more quiet combustion with a visible flame. Below this pressure ordinary combustion ceased altogether and combination occurred only by collision.

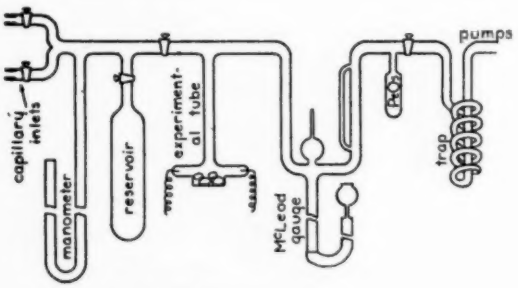


Fig. 1. Arrangement of apparatus.

The general arrangement of the apparatus in its final form is shown in Fig. 1, and the procedure was as follows. After the experimental tube had been carefully baked out and the system properly evacuated, several centimeters each of hydrogen and oxygen were introduced through capillary valves at the inlets as indicated. The ratio of hydrogen to oxygen was measured on the manometer during the filling process. The gaseous mixture was then pumped down to a pressure somewhat less than that at which explosion might occur, at which point the reserve reservoir was shut off so that the gas therein might be used for subsequent refillings of the experimental tube with identically the same mixture.

[6] Rusk, Phys. Rev. **29**, 907 (1927).

Owing to the fact that liquid air was not available to condense the water vapor which was formed, calcium chloride or phosphorus pentoxide was used in the experimental tube to absorb the water vapor formed there, and a freezing-solution trap was used to help keep mercury vapor from the tube. By this and by repeatedly washing out the tubes with the gases used, the mercury vapor was kept at a low pressure during most of the experiments, and the mercury lines frequently did not appear in the discharge until the readings were well under way. It is believed that any effect of mercury vapor was negligible.

Changes in the pressure of the gaseous mixture were read on a McLeod gauge of small size. The usual method was to run the discharge for ten seconds during each minute; the pressure readings being taken at the end of each minute.

Data and Results

Geissler-tube discharge and electrodeless discharge. Fig. 2 shows typical absorption curves obtained with the Geissler-tube discharge and the electrodeless discharge. The dashed line represents the level at which all the

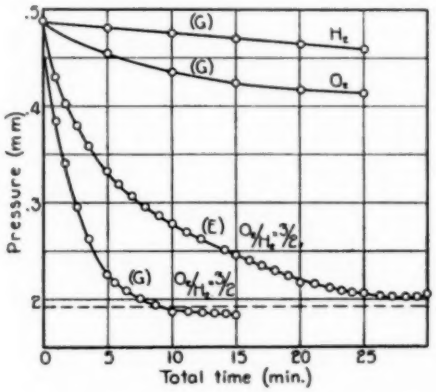


Fig. 2. Typical absorption curves obtained with Geissler-tube discharge, and electrodeless discharge. G, Geissler discharge, 10 sec. each minute. E, electrodeless discharge.

hydrogen should be used up, with a proportion of 3 parts of oxygen to 2 of hydrogen. As a check on these absorption curves similar sets of readings were taken with either oxygen or hydrogen alone as also indicated, and although a noticeable decrease in pressure usually occurred, as is common in such discharge tubes, it was not comparable with the effect of combination.

A considerable number of sets of readings were made with the Geissler discharge at total pressures as high as 5 mm. All these showed similar trends, and the curves were continuous with those at lower pressures.

The Geissler-tube current was usually maintained at 2 to 10 milliamperes for a period of ten seconds out of each minute, and the electrodeless discharge was maintained over similar periods of time. From the intensity of glow it was judged that the ionization was somewhat weaker on the average in

the electrodeless discharge, though no attempt was made to measure this directly.

Experiments with tubes of different sizes and shapes gave no direct evidence that the effect measured was due in any appreciable amount to catalysis at the walls of the tube. Experiments with Geissler tubes having large and small platinum electrodes gave no indication that the rate of combination was affected by the amount of platinum surface exposed at the electrodes. In the electrodeless discharge tube there was no metal present, and in equivalent volumes the decrease in pressure was logarithmic. Hence combination appeared to be largely a matter of gaseous collision.

Low-voltage arc. In Fig. 3 the absorption curves are compared for a tube with hot coated platinum filament and cold nickel anode, with and without the arc discharge. With the filament alone the combination due to catalysis

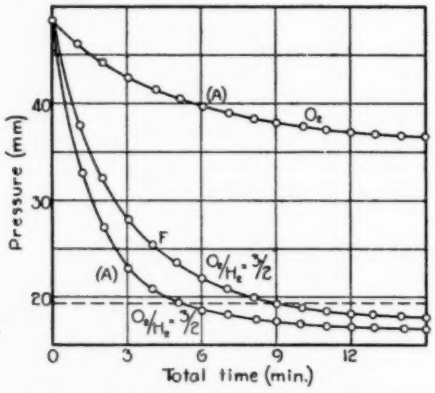


Fig. 3. Absorption curves for a tube with coated filament, with and without arc discharge. F, hot filament only: A, arc, 5 milliamperes.

only was very marked and with a five milliampere arc discharge at 74 volts the combination was somewhat greater. The difference presumably was due to the effect of the arc itself and was relatively small. As rapid combination due to catalysis set in quite regularly, with the filament used, at about 65°C (thermocouple measurement) it was impossible to eliminate this effect and get a satisfactory measure of the effect of the arc itself.

Effect of excess oxygen or hydrogen. When the curves for different ratios of oxygen and hydrogen are plotted logarithmically the result is seen in Fig. 4. For equivalent volumes the curve is practically a straight line, and the other curves for excess oxygen and hydrogen respectively, clearly indicate that excess oxygen accelerates the action and that excess hydrogen has the reverse effect. Lind has found similar results for excesses of oxygen and hydrogen in his alpha-ray experiments which he explains as being due to the greater specific ionization of oxygen. This correspondence would make it appear that the relative ionizations of the oxygen and hydrogen by electrons and alpha-particles are roughly the same. It is also of interest to note that the general trend of these curves is similar to those obtained by Langmuir

for platinum catalysis only, except that the lower curve was never found to be convex upward. The apparent agreement between degrees of ionization and rates of combination indicates the dependence of the latter upon the

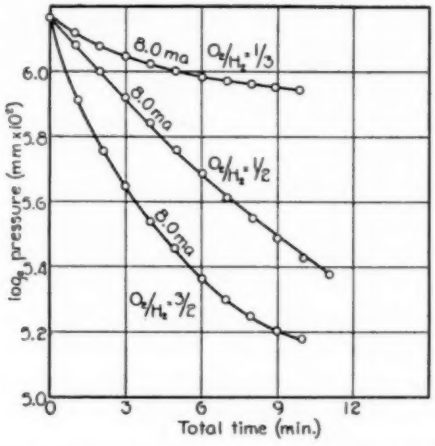


Fig. 4. Curves for various ratios of oxygen and hydrogen, plotted logarithmically.

former but the present data do not exclude an intermediate stage in the process and there appears to be some evidence for it.

Conclusions

From the simplest viewpoint, if the decrease in pressure is logarithmic we may write, by the usual formula for a decay curve, the total number of molecules at any time t is $N = N_0 e^{-\lambda t}$ where λ is the fraction disappearing in unit time. This may be written $\lambda = 3km/2N$ where N is the total number of molecules present; m is the total number of positive ions, or pairs of ions, liberated in unit time; and k is the number of gas molecules disappearing for each positive ion or pair of ions, assuming positives and negatives to be equal in number and that two molecules of water are formed when three gas molecules disappear.

For the curve to be straight when plotted logarithmically, λ must be a constant, and hence the product km must vary directly with the number of gas molecules present. Disregarding the problem of the relation of ionic density to the pressure of the gaseous mixture, it is possible to get an approximate upper limit to the value of k by assuming the current is an ionization current, carried chiefly by electrons, and that for every electron removed from the gas a positive ion remains. By this, 6.28×10^{15} positives would be liberated per second per milliampere. Obtaining λ graphically from Fig. 4 and solving for k, it appears that at 0.1 mm pressure in equivalent volumes of oxygen and hydrogen, and in a working volume of 400 cc, 0.12 molecules of water were formed for every positive ion or pair of ions liberated. This value is a little less than the average of several curves.

The above must be an upper limit as the actual density of ionization is doubtless greater than that implied in the above assumption, though it may

not be much greater at the lower pressures. For k to approach the value 3.6 obtained by Lind at higher pressures it must increase with increasing pressure as it appeared to do in the present experiment. Were the proportion a direct one k would have the value 1.8 at 1.5 mm pressure. At this pressure the time between collisions is 5×10^{-8} sec. in hydrogen which is the usual value for the life of an excited hydrogen atom. It appears from this that when one positive ion forms on the average one molecule of water the time between collisions must at least be very close to the accepted value of the life of excitation of hydrogen.

If k were always less than unity the ions themselves might well be assumed to combine directly, but when k becomes greater than unity it appears necessary to assume either a secondary process or the possibility that the combination is due to cluster ions. The work of Mitchel adds credence to the former theory. It is not assumed, of course, that combination necessarily occurs always in exactly the same manner, and Barton and Bartlett[7] have given us a partial picture of the reverse process in which water vapor is broken up into a variety of component ions some of which are evidently due to secondary processes. From a consideration of these data it appears probable that combination may be due, in part at least, to some type of excitation of the atom or molecule which is secondary to the process of ionization, and whose life may be directly comparable to that of the optically excited hydrogen atom.

The above measurements were made with the help of Mr. Harold Zahl for whose assistance acknowledgment is herewith made.

NORTH CENTRAL COLLEGE,
NAPERVILLE, ILLINOIS.
November 29, 1927.

[7] Barton and Bartlett, Phys. Rev. 31, 822 (1928).

THE MEASUREMENT OF ULTRA-VIOLET QUANTA BY FLUORESCENCE PHOTOMETRY

By Wm. T. Anderson, Jr., and Lester F. Bird

Abstract

The relative intensities of monochromatic ultra-violet light determined throughout the ultra-violet mercury spectrum by the use of a fluorescence photometer employing widely different chemical substances were shown to check the intensities of the light given by the thermopile. The agreement between the photometric and thermopile measurements indicates that both methods may be employed for measuring accurately the energy in the ultra-violet region.

Introduction

THE vital importance of the ultra-violet portion of the spectrum and quanta to the physician, biologist and chemist has greatly stimulated interest in quanta measurements. At present, the thermopile and galvanometer are satisfactorily, and almost exclusively, used for such measurements. There exists a need for a method which can measure ultra-violet quanta directly, and which responds to fewer quanta than the average thermopile. It would also be very advantageous to be able to make quantitative ultra-violet measurements without the necessity of the precautions required in radiometry, e.g., freedom from stray magnetic fields, elimination of stray visible and infra-red radiations, etc.

The phenomenon of fluorescence has been selected as a suitable quantum reaction for measuring ultra-violet light intensity. All fluorescent reactions, however, do not fullfil the requirements. In order to be satisfactory, the emitted fluorescence light must be proportional to the intensity of the absorbed exciting radiation. The spectral energy distribution of the fluorescence light must be independent of the intensity and wave-length of the incident light. The fluorescent material must remain essentially unchanged throughout the investigation.

Three widely different fluorescent materials were employed: (1) an inorganic substance, uranium glass; (2) a dyestuff, fluorescein; (3) an alkaloid, esculin, all of which absorbed completely the ultra-violet under the experimental conditions. These three substances fluoresce brilliantly on exposure to all wave-lengths of the ultra-violet. No chemical change is known to take place in the uranium glass, the glass being apparently unchanged after many hours of exposure. The esculin and fluorescein are known to be affected by continuous irradiation with ultra-violet light, but within the time of the investigation and for the intensities of light employed the alteration in the chemical composition is negligible.

The ultra-violet light received by these materials was converted into visible light of the regions comprising the blue, green and yellow. Since the exciting radiation was completely absorbed by these materials, in each case,

all the energy should be converted. The visible light emitted by the fluorescent materials was easily measured by photometric methods using a monochromatic green filter. Errors in the observation of the fluorescence light, however, existed when the ultra-violet radiations penetrated appreciably since in the case of the uranium glass and fluorescein only the light emitted by the irradiated surface was viewed. Light produced beneath the surface was not effective because of scattering and absorption. The method employed in viewing the esculin included almost all of the light produced. The penetrations for all three substances are negligible for wave-lengths shorter than 3340 Angstrom units.

Outline of Investigation

The photometer was arranged in the usual form employing the inverse square law of illumination. A frosted 100 watt nitrogen filled lamp was mounted on a car whose motion was guided by a track. The intensity of

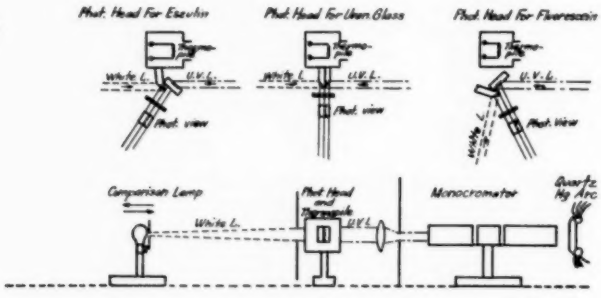


Fig. 1. Photometer and thermopile for ultra-violet light measurement.

the light could be adjusted by means of a diaphragm located immediately in front of the lamp when the maximum motion was not sufficient to cover the range of illumination required. A block of opal, or milk, glass was used as the illuminated comparison screen. The entire apparatus was arranged so that the illumination of the comparison screen varied inversely as the square of the distance to the diaphragm. The fluorescent material and the block of opal glass were arranged in each case as a photometer head so that the white light from the opal glass and the fluorescence light could be viewed side by side with an almost invisible edge between them. To the eye, the light from the illuminated screen and from the fluorescent material appeared as two elongated rectangles side by side and of equal size. The white light from the milk glass and the colored light from the fluorescent material were viewed through a monochromatic green light filter so that both sources of light appeared to the eye to be of the same color. Owing to the high sensitivity of the eye to green light, balances could be made with considerable accuracy.

A quartz monochromator was used to illuminate the fluorescent material. The light source for the monochromator was a Hanovia scientific quartz

mercury lamp. The mercury spectrum is emitted by this lamp and has strong lines throughout the near and middle ultra-violet regions. The monochromator provided ample separation of the wave-lengths so that practically pure monochromatic light was secured. During the experiment the monochromatic ultra-violet light was arranged to illuminate the fluorescent material and a balance of the emitted green light was secured on the photometer.

Since the measurements of the response of the fluorescent materials with respect to the incident radiation were purely relative, and the differences in the degree of reflection, of the exciting radiation at the surfaces, were slight throughout the range of wave-length studied, reflection introduced negligible errors.

The uranium glass was prepared in a block about 1.5 inches square with one edge bevelled to 45° and left rough-ground. The milk glass block for the comparison screen was prepared in a similar manner. The ultra-violet light was arranged to illuminate the bevelled edge of the fluorescent glass. The glass blocks were separated with rough finish black paper. Covering either source of illumination caused the corresponding blocks to disappear from the photometer view completely.

Solutions of the esculin and fluorescein were employed in suitable quartz bottles. These bottles were rectangular in form with ground and polished faces. The solution of esculin being clear, was entirely transparent to its own fluorescence light so that this light could be viewed from the back side of the bottle. The fluorescein, of the concentration used, was not transparent to its own fluorescence light and so its light had to be viewed on the irradiated face. This procedure introduced some error since the wave-length 3660 Angstrom units penetrated into the solution slightly and because of absorption and scattering all the light produced was not available for measurement. The light of wave-length 3660 Angstrom units also penetrated uranium glass very readily but the use of a rough-ground surface seemed to limit the penetration in this experiment so that but little error was introduced.

The thermopile and photometer head were mounted side by side on a little car so arranged that the exciting ultra-violet could be readily directed on either the thermopile or the photometer head. The car was guided by a track and stops were adjusted so that the instruments were always returned to the same spot.

The intensity of the band of ultra-violet light was measured first on the thermopile, then by the fluorescence photometer, numerous checks were made and two observers alternated at reading the photometer, their average results being recorded.

Measurements of the fluorescence of these three substances demonstrated that they all responded equally for all wave-lengths, i.e., there was no selective action. When the intensity of the fluorescence light, measured photometrically, was plotted against wave-length, the curves for all three substances were exactly the same shape and could be made to coincide by employing the proper constants. The constants were necessary because the

TABLE I. *Epxerimentol data.*

Wave-length	Distance of screen from lamp	Distance²	k / (Dist.)²	Galvanometer deflection
	Uranium glass ($k = 1.109 \times 10^4$)			
2537	18.8	353	31.4	27.0
2650	19.3	373	29.7	29.0
2800	31.3	980	11.3	14.0
2967	29.3	757	14.65	14.0
3130	11.55	133.3	83.2	75.0
3660	9.42	88.7	125.0	123.0
	Esculin solution ($k = 2.34 \times 10^4$)			
2537	28.12	792.0	29.6	30.0
2650	30.25	917.0	25.6	29.0
2800	40.7	1653.0	14.16	10.0
2967	33.5	1124.0	20.8	21.1
3025	24.75	614.0	38.1	38.0
3130	17.5	306.0	76.5	80.0
3660	13.43	180.5	129.6	127.0
	Fluorescein solution ($k = 2.34 \times 10^4$)			
2537	25.43	648.0	36.1	41.0
2650	27.25	744.0	31.4	29.0
2800	40.5	1640.0	14.27	16.0
2967	32.31	1045.0	22.4	24.0
3025	25.75	644.0	35.2	34.0
3130	18.0	324.0	72.3	78.0
3660	16.56	274.0	85.5*	125.0

* Radiation not totally absorbed on the surface.

photometer employed only the green component of the fluorescence spectra for the intensity measurements and the energy distribution in the fluorescence spectra of these three substances was not the same. The constants in any

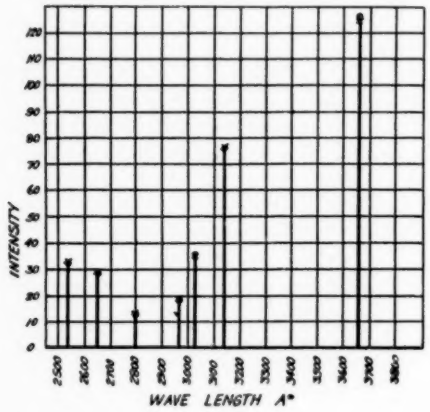


Fig. 2. Measurement of the ultra-violet lines of the mercury arc spectrum by two methods, showing the close agreement for all frequencies. Circles are measurements with the photometer; crosses are measurements with the thermopile.

case merely determine the reference light strength for the photometer and can be any value without affecting the proportionalities in the various

regions. When these curves were compared with the curve obtained by plotting the galvanometer deflections against wave-length, they were found to have the same shape, and a proper constant made the galvanometer deflection coincide with the photometer readings indicating that the thermopile and the fluorescent material measure the same relative intensity of ultra-violet light.

Conclusions

The relative intensities of fluorescence excited at various wave-lengths in the ultra-violet are in remarkably close agreement, indicating that the efficiencies of conversion of ultra-violet into visible light are quite uniform. In view of the widely different chemical constitution of these substances and their agreement in responding to the ultra-violet wave-lengths it is evident that the fluorescence of these substances gives a true relative measure of the ultra-violet quanta received.

Table II. *Comparison of photometer readings and galvanometer deflections.*

	Values of $100 \times \frac{\text{photometer reading}}{\text{galvanometer deflection}}$			
Wave-length	Uranium glass	Esculin solution	Fluorescein solution	Average percent
2537	116.2	98.8	88.0	101.0
2650	97.6	88.4	108.2	98.1
2800	80.8	141.0	89.1	100.2
2967	104.5	98.8	93.3	98.9
3130	111.0	95.6	103.4	99.8
3660	101.5	102.0		101.7

Since the relative intensity of the monochromatic ultra-violet light at the various wave-lengths as determined by the thermopile agrees so satisfactorily with that obtained by the photometric measurements of the fluorescence light emitted by these three substances, it seems certain that both methods correctly measure the quanta received at ultra-violet wave-lengths. The fluorescence photometer and the thermopile may be satisfactorily employed for measuring quanta.

The authors wish to acknowledge the interest and many helpful suggestions of Dr. W. W. Coblentz of the Bureau of Standards, and Professors K. T. Compton and H. S. Taylor of Princeton University.

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Hanovia Chemical and Mfg. Company, Newark, N. J.
May 7, 1928.

ON THE PRECISE DETERMINATION OF THERMAL CAPACITIES WITH PARTICULAR REFERENCE TO THAT OF MOLYBDENUM

By T. E. Stern

Abstract

It was found that a *Bunsen ice calorimeter* modified by the addition of a silvered vacuum jacket was capable of yielding precise values of the total heats of substances. The falling body was contained in a metal capsule to eliminate errors due to radiation and convection during fall. Thermal contact was established in the calorimeter by a copper cup, containing water or mercury, and surrounded by water. The probable error of a single observation of the motion of the mercury thread caused by a hot body was about one part in one thousand. By this method the specific heat of molybdenum was found to be $c_p = .05973 + .00001619t$ mean cal./gm °C between the temperatures of 0°C and 444.5°C.

Apparatus and Procedure

A BUNSEN ice calorimeter was used, modified by the addition of a vacuum jacket D silvered inside, except for a narrow window. The central tube A contained a cylinder of copper C, supported by a spring, and having a conical cavity in its upper surface. The region B around the central tube contained water as far down as G, below which there was mercury. The latter communicated by way of the tube H and the steel chamber E with a horizonal glass capillary, not shown.

The 100° heater, likewise not shown, was a tube containing the body to be heated, surrounded by a steam jacket. The whole was well insulated with felt.

The sulfur point heater consisted essentially of two coaxial steel tubes I and J, containing sulfur between them at the bottom. The inner one was closed at the top by a stopper O through which a wire containing the heat insulator M and supporting the object N was passed. The bottom of I was protected by the shield L at all times except during the dropping of the body N. Heating coils outside J surrounded the sulfur. The whole apparatus was enclosed in a metal covering K, being separated from it by an insulating material. The cover P fitted loosely over the region between I and J, preventing excessive escape of vapor and at the same time maintaining atmospheric pressure in the region.

The following sources of error had to be considered: (1) Lack of uniformity of bore in the capillary. (2) The creep of the mercury thread at all times due to the differences between the temperature of the ice in the calorimeter and the ice in the bath outside. (3) The loss of heat by radiation and convection during the fall of the body. (4) The dependence of the density and possibly also of the latent heat of fusion of ice upon the

manner and recency of its freezing. (5) The evaporation during fall of the water used for calibrating the calorimeter. (6) Errors of thermometry. (7) The loss of heat by convection and radiation after the dropping of the object into the calorimeter.

The capillary was 70 cm long, and was graduated in millimeters. It was studied by three mercury threads of lengths respectively 35 cm, 7 cm, and 3.5 cm. The errors due to lack of uniformity of bore were determined by observing the lengths of these threads at different positions by travelling microscopes. All readings were corrected for these errors. The vacuum jacket, which separated the calorimeter from the ice bath, reduced the creep to one or two millimeters per hour. It was regular, and the mean

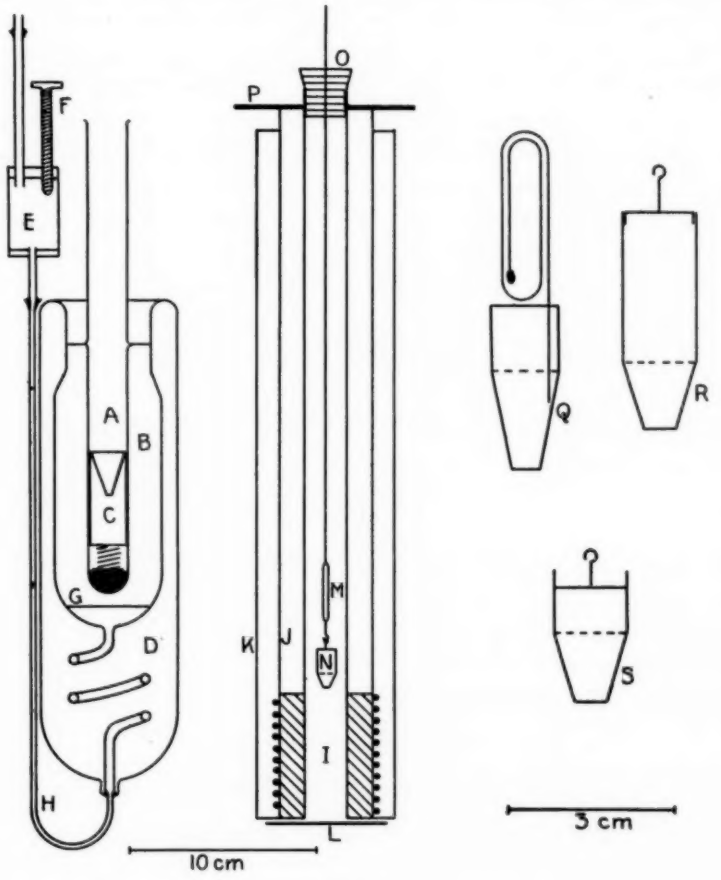

Fig. 1.

creep during an experiment was found by observations before and after, and corrected for. The falling object was always enclosed in a metal capsule. Upon subtracting from the motion thus produced that caused by the empty capsule when dropped at the same temperature, the motion which would be caused by the body alone, free from errors due to radiation and

convection during fall, was obtained. Ice at 0° should eventually reach a state free from interal strain; and it was found, providing the ice sheaths were not used until four days after being formed, that consistent results could be obtained. To prevent evaporation, the water at 100° used for calibration was contained in a soldered capsule *Q*. As in the former case, this also served to eliminate errors due to radiation and connection during fall. The use of the steam and sulfur heaters freed the writer from the necessity for thermometry.

The sulfur point was taken to be 444.5°C after Eumorfopoulos,[1] Callendar,[2] and others. A pressure coefficient[3] of 0.09°C/mm was used. There was a possibility that the region inside *I* did not have the temperature of the boiling sulfur; this matter was tested by a comparison with a standard shielded sulfur point apparatus by means of a thermocouple. The difference was about 0.25°C, which would introduce a negligible error. When water was used inside of the copper cup *C*, the cooling was too rapid to permit much loss by convection; but when mercury was used, especially at the high temperature, the cooling was slower, and there was an opportunity for such loss. The experimental results, however, were the same. It was accordingly inferred that the loss was very slight. Geometrical considerations showed that of the whole small quantity of heat radiated by the object in the calorimeter, only about one-tenth could escape altogether from the apparatus. The ice bath came up as far as *F*; above this the tube leading to the capillary was surrounded by melting ice. Errors due to variations of temperature of the capillary were corrected for. The calorimeter was designed to work best for 240 calories, and for this quantity of heat the probable error of a single observation of motion was 1/1000 of the whole.

Results

Some specimens of molybdenum, in the form of cylinders 0.2 inch in diameter, were kindly furnished by the General Electric Company, who stated the purity to be about 99.97%. It was found that 0.5611+0.0003 mean calories caused a motion of one corrected scale division. The mean specfic heats of molybdenum were found to be

$$c_{0-100} = 0.06054 \pm 0.00006 \text{ mean cal/gm } °C.$$

$$c_{0-441.5} = 0.06333 \pm 0.00010 \text{ mean cal/gm } °C.$$

The constants in the equation $c = a + bt$ were accordingly found to be 0.05973+0.00015 and 0.00001619+0.00000068 respectively.

Previous determinations by various investigators differed widely. Fig. 2[4] embodies almost all of the previous results between −100°C and 300°C.

[1] Eumorfopoulos, Proc. Roy. Soc. **A81,** p. 339 (1908).

[2] Calldendar, Proc. Roy. Soc. **A83,** p. 106 (1909).

[3] Trav. et Mem du Bureau intern. des Poids et Mes. **12,** 75, 1900.

[4] Reproduced from Physical Review **30,** 332 (1927).

This determination was suggested by Professor K. T. Compton, for the purpose of securing satisfactory values of the specific heat of molybdenum,

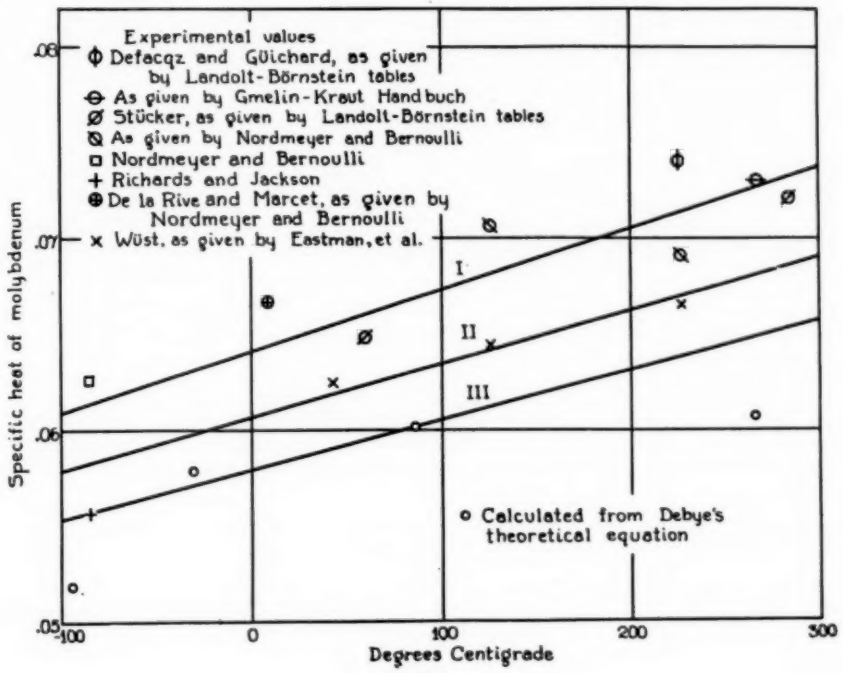

Fig. 2.

needed for the determination of the heats of condensation of electrons. The writer's thanks are due him for his valuable suggestions.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.
May 10, 1928.

THE DIELECTRIC CONSTANT OF AIR AT RADIO FREQUENCIES

By A. B. Bryan and I. C. Sanders

Abstract

A radio frequency method has been used to measure the dielectric constant K of dry air free from CO_2, the value obtained being 1.0005893 for standard conditions of temperature and pressure. The probable error in $K-1$ due to accidental variations is 0.34 percent. The method is a modification of the usual heterodyne beat arrangment. Capacity changes produced when the pressure in the test condenser is changed are compensated by a suitable condenser in parallel. The beat note frequency is compared with that of a fork by means of Lissajous' figures. The test condenser is made of invar to avoid temperature effects. Short connecting wires are used to minimize lead-inductance effects. A few preliminary measurements made with a large direct current voltage superimposed on the high frequency voltage across the condenser indicate no change in the dielectric constant of air, hydrogen, or ammonia. There is some indication that a discharge through the gas decreases its dielectric constant but the effect is probably spurious.

Introduction

THE various radio frequency methods for measuring the dielectric constant of a gas are best suited for relative determinations, in which the dielectric constant is obtained in terms of that of some standard gas, usually air. For this reason it is obviously desirable that the dielectric constant K of air be accurately known. The older experiments of Boltzmann[1] and of Klemencic[2] have established the value of K with fair accuracy: their values of 1.000590 and 1.000586 are in good agreement. But there has arisen a possibility that these values, obtained with the older methods, may not be true at radio frequencies because the two radio frequency values 1.000540 and 1.000572, obtained by Fritts[3] and Zahn[4] respectively, are considerably lower. Carman and Hubbard,[5] using a method of the older type, have recently obtained a value 1.000594 which may be considered in agreement with that of Boltzmann. In the present work a new radio frequency measurement is made in an effort to settle the discrepancy between the two types of experiment. There is no theoretical reason why the value of K should be abnormally low at radio frequencies and it has been more generally believed that the radio frequency measurements were inaccurate because of the calibration difficulties involved. This belief is confirmed by the result of the present experiment which is in agreement with the original value of Boltzmann.

[1] L. Boltzmann, Wien. Berichte **69**, Part 2, 795 (1874).
[2] J. Klemencic, Wien. Berichte **91**, 712 (1885).
[3] E. C. Fritts, Phys. Rev. **23**, 345 (1924).
[4] C. T. Zahn, Phys. Rev. **24**, 400 (1924).
[5] A. P. Carman and K. H. Hubbard, Phys. Rev. **29**, 299 (1927).

Apparatus

The experimental arrangement as shown in Fig. 1 is in many ways similar to those previously used. Capacity changes produced when the air pressure in the test condenser C is changed are compensated by a suitable condenser C_c in parallel, so as to keep constant the total capacity and the frequency of the radio frequency oscillator A to which the condensers are connected.

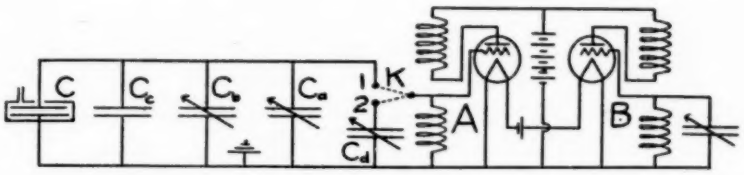

Fig. 1. Arrangement of circuits.

Constancy of frequency is indicated by a constant beat note between A and a second oscillator B. The oscillators use UX201A tubes and have a common plate battery of two 45 volt units and a common 8 volt lead storage filament battery.

The beat note between the two oscillators is obtained by means of a separate arrangement consisting of a small loop antenna, a detector and two stages of amplification connected to a loud speaker unit. This part of the apparatus is at some distance from the oscillators and no reaction on them has been detected. The frequency of the beat note is compared with that of a 300 cycle electrically driven fork by means of Lissajous' figures obtained when a beam of light is reflected by a small mirror attached to the vibrating loud speaker element and then by a second mirror attached to the fork.

A key K is used so that either condenser C_d alone or the system of four condensers C, C_a, C_b, C_c in parallel may be connected to oscillator A. C_a and C_b are similar General Radio Type 222 Precision condensers, each having a maximum capacity of about 1500 mmf. The condenser scale has 25 divisions and a slow motion screw is provided so that readings may be made directly to one hundredth of a division. These condensers are well designed electrically and mechanically. The ebonite insulation is so arranged as to minimize dielectric losses and no flexible leads are used. C_d is a good variable air condenser of another type.

C_c is a specially constructed cylindrical condenser. A length of heavy tube forms the insulated plate and a half-inch rod, running along the axis of the tube, is connected to earth. A long sleeve, fitting the rod closely, can be moved into the tube by a micrometer screw, thus increasing the capacity. A motion of one cm produces a calculated capacity change of 0.254 mmf. The condenser is shielded by an outside cylindrical case, ebonite insulation being used where necessary. All metal parts are accurately made of brass. Readings are taken on the central portion of the scale to avoid end effects.

The test condenser C is made as shown in Fig. 2. The figure is to scale except that for the sake of clearness a condenser with only five plates is

shown. There are actually thirteen circular plates, the seven earthed plates being 9.4 cm in diameter and the six insulated plates 4 mm less. The plates are 1 mm thick and the spacing about 1 mm. The capacity is approximately 753 mmf. Each of the two sets of plates is held together by three equally spaced bolts around the edge with metal separators between the plates. Two of these six bolts are shown in the figure. The insulated set of plates is supported by three short sections of quartz tubing, one of which is shown at *Q*. The sides of the condenser are closed by a short length of large thin tubing which fits the earthed plates closely as shown. A half-inch hole in the center of each of the plates except the bottom one allows the air to pass freely into all parts of the condenser. The condenser is made entirely of invar. The outer case is of brass, all joints being made tight with sealing wax. The case is connected to earth through a wire soldered to its side. The small mercury cup connection at *M* prevents any transmission of force to the condenser due to a slight yielding of the top of the case when the air pressure is changed. The screw connector at *A* is joined by a short length of

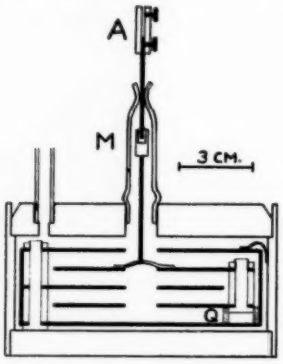

Fig. 2. Design of the test condenser.

wire to a similar connector just above and thence to the other condensers. The test condenser is disconnected when desired by moving this short length a small distance up into the upper connector.

All the condensers are of course shielded by their cases. No other shielding is needed. The several condensers and the key *K* were controlled from a distance by a suitable arrangement of threads.

The air used is passed through a solution of KOH to remove CO_2 and then through a tube of $CaCl_2$ and one of P_2O_5 to remove water and is then stored in a reservoir containing P_2O_5. From this reservoir it passes through a pump into the condenser. This pump consists of a large bulb into which mercury can be forced from the bottom. At the top is a two-way stop cock providing connection to either the condenser or the reservoir. The air can thus be pumped either way and the pressure in the condenser can also be quickly changed back and forth between two definite values by filling or emptying the bulb. Pressures were measured with an open mercury manometer read with a cathetometer. The motion of the mercury in the pump or manometer

produces no effect on the oscillators. Temperatures are measured to one twentieth of a degree with a thermometer in contact with the test condenser case.

Experimental Procedure

C_a and C_b are set at any desired value and then, with the key in position (1), the B oscillator is adjusted until a 600 cycle beat note and consequently a 2:1 Lissajous' figure is obtained. The air pressure in the condenser is then changed from its initial value P_1 to a second value P_2 and C_c is changed by an amount δC_1 so that the total capacity is the same as before and the 2:1 figure is restored. Then assuming that $K-1$ is proportional to the density of the gas, δC may be calculated from the relation $\delta C=\delta C_1(T/273)76/(P_1-P_2)$ where δC is the value which would be observed for a pressure change of one atmosphere at a temperature of 0°C and T is the absolute temperature at which the measurement is made. $K-1$ is found by dividing this δC by C, where C is that part of the capacity of the test condenser which changes when the air pressure is changed. The accurate determination of C in the same units as δC is a matter of some difficulty and will be considered under "calibration."

There is always a tendency for the beat note to change slowly because of changes in the oscillator batteries or in the temperature and a change of this sort while the gas pressure is being changed can lead to a serious error in δC. This slow drift of the beat-frequency is reduced by the use of common plate and filament batteries and by working in a basement room where the temperature is quite steady. Error due to this effect is further reduced by constant use of the key K and condenser C_d in the following way. C_d is originally set so that its capacity is equal to the sum of the capacities of the other four condensers and the 2:1 figure is obtained when the key is in either position (1) or (2). Later the key is frequently pulled over to position (2) and the 2:1 figure restored if necessary by a slight adjustment of oscillator B. The method may thus be considered as one in which the sum of the capacities of C, C_a, C_b and C_c is kept equal to the capacity of C_d, the oscillators being used merely to indicate when this equality exists. It is realized that this is not a strictly accurate view since switching the key over probably introduces slight changes in the inductance and resistance of the circuit. But even if this is so the accuracy of the result is not seriously affected.

Calibration

As previously explained, the capacity C of the test condenser must be measured and the result expressed in scale divisions of the cylindrical condenser C_c. To do this a step-by-step calibration curve of C_b is first obtained, the step used being the interval 22.0 to 23.0 on C_a. C_b is set at 25.0 and C_a at 22.0. Then C_a is increased to 23.0 and C_b decreased until the total capacity is the same as before. This process is repeated, a continuous series of scale readings on C_b being obtained which represent equal capacity intervals. A calibration curve may then be plotted for C_b with the capacities in these

arbitrary units as ordinates and the scale readings as abscissae. One of these arbitrary units is about 59.5 mmf.

The next move is to determine the capacity of the test condenser C by comparison with C_b. C is disconnected and C_b increased to restore the frequency to its original value, the capacity of C being equal to the increase in C_b. A series of readings taken in this way is shown in Table I. The scale

TABLE I. *Data for determining capacity of test condenser.*

C_a (scale rdg.)	C_b (scale rdg.)	λ (meters)	C_b' (scale rdg.)	$C_b'-C_b$ (arb. units)
0	6.960	336	19.354	12.734
0	7.986	342	20.301	12.725
0	8.000	342	20.318	12.729
0	9.002	350	21.255	12.723
12.0	6.996	415	19.399	12.746
12.0	7.970	421	20.300	12.741
12.0	8.000	421	20.332	12.744
12.0	8.993	428	21.261	12.739
25.0	7.020	495	19.429	12.753
25.0	7.966	498	20.300	12.745
25.0	7.997	500	20.337	12.752
25.0	9.000	502	21.278	12.751
				mean 12.740

reading of C_a, the initial reading of C_b and the corresponding wave-length are shown in the first three columns. The fourth column gives the second reading of C_b after the test condenser is disconnected. The last column gives the increase in capacity of C_b, expressed in the above mentioned arbitrary units and obtained from the two readings of C_b and its previously obtained calibration curve.

The total capacity of the test condenser is thus 12.740 arbitrary units. A small part of this total capacity does not have the air in the condenser as its dielectric. The capacity through the three quartz ring insulators may be calculated and is 4.5 mmf. The external capacity to the screw connector A (see Fig. 2) and the wire below it is estimated at 1.2 mmf. When this correction of 5.7 mmf or 0.096 arbitrary units is subtracted the corrected value $C=12.644$ arbitrary units is obtained. The error made in estimating this correction is probably not greater than one mmf or 0.13 percent of C

Finally this value of C must be expressed in scale divisions of the cylindrical condenser C_c, that is, the number N of C_c divisions in one arbitrary unit of capacity must be found. This is done by determining the capacity change necessary to produce a certain frequency change when either C_c or C_b is varied by a small amount and then equating the capacity changes in the two cases. The results are shown in Table II. A particular trial, the first in the table, will be described in detail. C_a and C_b are set at 25.0 and 19.6 respectively. It is then found that when C_c is changed from 5.998 to 9.982 and then to 11.312 the corresponding beat notes are 600, 525 and 500 as indicated by the 2:1, 7:4 and 5:3 Lissajous' figures in the three cases. The three condenser settings are repeated several times and the values given are

means. Since the capacity and frequency changes are proportional for small changes the above data give $\delta C_c = 5.316$ scale divisions on C_c, where δC_c is the change in C_c for a 100 cycle frequency change, and show incidentally that the scale of C_c is linear within the limits of experimental error. C_c is then set at about the mid-point of the range over which it has been varied and oscillator B is adjusted until a zero beat note is obtained. C_b is then changed, a setting on either side of the original 19.6 being found where the beat note is 2100 cycles, as indicated by a 7:1 figure. The interval between these two settings, corresponding to a 4200 cycle frequency change, is 0.9068 divisions on the scale of C_b, as tabulated under δC_b. In this case the frequency change is so large that it is not quite permissible to assume that the frequency and capacity changes are proportional and it may be shown that the quantity 0.9068 must be divided by a correction factor $(1+3\delta n/2n)$, where $\delta n = 2100$ and n is the frequency at which the trial is made or 533000 in this case. S, in the seventh column, is the slope of the previously obtained calibration curve in condenser divisions per arbitrary unit. The curve has been plotted in a special manner to make possible an accurate determination of S at any point. At the point 19.6 the value of S is 0.948 and δC_b must be divided by this value to convert it to arbitrary units. Finally, it will be seen that N in the last column is given by the relation $N = 42 S \delta C_c (1+3\delta n/2n)(1/\delta C_b)$.

When the previously obtained corrected value of C in arbitrary units is multiplied by the mean value of N from Table II it is found as the final result of the calibration that $C = 2957.5$ divisions on the scale of the cylindrical condenser C_c.

TABLE II. *Data for determining the capacity of the test condenser in terms of C_c.*

C_a	C_b	δC_c	δC_b	n	$(1+3\delta n/2n)$	S	N
25.0	19.6	5.316	.9068	533000	1.006	.948	234.8
25.0	22.0	5.628	.9639	522000	1.006	.948	233.9
25.0	18.0	5.008	.8687	540000	1.006	.988	234.6
0	7.5	1.359	.2496	862000	1.004	1.021	234.4
0	8.5	1.443	.2628	845000	1.004	1.011	234.1
*0	20.6	1.342	.2279	862000	1.004	.948	235.4
*0	21.6	1.431	.2441	845000	1.004	.948	234.3
12.0	7.5	2.337	.4321	704000	1.005	1.021	233.0
*12.0	20.6	2.321	.3987	704000	1.005	.948	232.8
12.0	8.0	2.392	.4387	700000	1.005	1.015	233.5
*12.0	21.0	2.368	.4057	700000	1.005	.948	233.4
12.0	7.0	2.283	.4223	714000	1.004	1.023	233.3
12.0	7.5	2.341	.4309	704000	1.005	1.021	234.0
12.0	8.0	2.392	.4380	700000	1.005	1.015	233.9
12.0	8.5	2.441	.4468	698000	1.005	1.011	233.0
							mean 233.9

* Inidicates test condenser disconnected.

It may appear that a more direct determination of N could be made by merely increasing C_b and decreasing C_c so as to keep the frequency constant. But this involves measuring a very small motion of C_b because the range of C_c is very small and trials have shown that the required accuracy cannot be obtained because of some very slight looseness of the condenser bearings.

A direct comparison of this sort would require a condenser for which the capacity at a given setting is reproducible with almost impossible accuracy.

A mirror mounted directly on the moving plates and a telescope and scale have been used to test the driving mechanism of C_b. It has been found that the angular rotation for a complete division is accurately the same at all points on the scale but that there is a slight irregularity in the readings between divisions due to some slight defect in the slow motion screw. And so in the above work, where extreme accuracy is required, the values of δC_b are measured with the teslescope and scale.

Results

In Table III are shown the results of eight consecutive trials for air made at various times during one week. δC_1 is the observed change in C_e for a pressure change (P_1-P_2) and an absolute temperature T and δC the change for a pressure change of one atmosphere at 0°C, calculated from δC_1 as previously explained. The values are in scale divisions of condenser C_e. Each trial is obtained by changing the pressure from P_1 to P_2 and back again to P_1 several times and observing the corresponding readings of C_e so that

Table III. *Change in capacity of test condenser when pressure of air is changed.*

T	P_1-P_2	δC_1	δC
297.9	57.40	1.205	1.741
297.9	57.40	1.200	1.734
292.7	57.35	1.228	1.745
292.7	57.29	1.235	1.757
292.7	56.51	1.206	1.739
291.0	57.50	1.240	1.747
291.4	57.58	1.235	1.740
291.8	57.67	1.237	1.742
			mean 1.743

each trial is really the mean of several. For the third, fifth and seventh trials C_a is set at 12.0 on its scale and the wave-length is 421 meters. For the others C_a is set at zero and the wave-length is 342 meters. C_b is set at 8.0 for all trials. As a matter of convenience the two pressures used are approximately the same in all cases, P_1 and P_2 being about 76 cm and 18 cm respectively. Preliminary results have shown that the value of δC is not dependent on the particular pressures used.

When the mean value of δC from Table III is divided by the value $C=2957.5$ C_e divisions previously found, the value $K-1=0.0005893$ for dry air free from CO_2 at a pressure of one atmosphere and a temperature of 0°C is obtained as the final result.

Sources of Error and Experimental Difficulties

The value of $K-1$ has been calculated from the average values of the three quantities tabulated in the last columns of the three tables and the probable error due to the accidental variations in these quantities is 0.34 percent. There is a possible constant error due to the somewhat uncertain

correction which has been used to allow for the test condenser capacity which does not have the gas as its dielectric. This error has been minimized by making the total capacity of the test condenser large and has already been estimated as not greater than 0.13 percent.

Two of the experimental difficulties encountered may be mentioned. The first was that in some cases the initial rise in capacity when air was admitted was followed by a slight continued increase so that the capacity did not reach a steady value until several minutes after the pressure had become constant. Simultaneous measurements with a thermocouple showed a similar rise of the temperature of the condenser plates when air expanded into the condenser and this may have been the cause of the disturbing effect. However, the temperature rise was apparently too small to be entirely responsible and some yielding of the condenser was probably also involved. At any rate the trouble was overcome when, after several other designs had been found defective, the invar condenser which has been described was made.

The second difficulty is due to the inductance of the wires connecting the condensers. When the condenser is mounted in a liquid bath to permit temperature variations, as was done at one time in the present work, the leads to it must have considerable length and inductance. Measurements made under these conditions gave values of $K-1$ which showed a definite increase with frequency in spite of the fact that an apparently suitable correction for the lead inductance was applied. It is believed that corrections of this sort, made with the usual simplifying assumptions of localized inductances and capacities and negligible resistances, are somewhat doubtful unless subject to direct experimental test. Of course it should be possible to overcome the difficultly if all possible inductances, capacities and resistances were taken into account but apparently a simpler and more direct result is obtained by using short leads of negligible inducdance, and this has been done. The fact that the results which have been given show no dependence on the frequency indicates that the lead inductances are negligible.

This question of lead inductance has also been considered by Watson[6] in a paper which has recently come to the writers' attention. Watson uses a radio frequency method to measure the dielectric constants of several gases, including air, and devotes speacial attention to obtaining accurate absolute values. He applies corrections for lead inductance which are apparently satisfactory in that his results do not in general show any dependence on the frequency, although he does report a very slight increase with frequency in the value of K for CO_2. Watson's method of correcting for lead inductance is essentially the same as that which has been found inadequate in the present work and the fact that he finds it satisfactory may possibly be due to his use of a test condenser of rather small capacity (133.3 mmf). It is obvious that at a given frequency the impedence due to the inductance in the connecting wires to a condenser is a smaller part of

[6] H. E. Watson, Proc. Roy. Soc. **117A**, 43 (1927).

the total impedence when the capacity is small and any error in estimating this impedence is less serious. For this reason the use of a small test condenser is an advantage, although it is a decided disadvantage for other reasons. Watson's work has been carefully done and the fact that his value 1.000601 for air is apparently a little too large, as compared with previous results, serves to emphasize the difficulties of this sort of experiment.

Watson also points out that a change in the amplitude of the radio frequency current may change the capacity of a condenser because of the changing electrostatic attraction between the plates. The method used and the results obtained in the present work indicate that this effect is not a source of error. The experiments described below also show that the effect of electrostatic forces is so small that no appreciable effect would be produced by such amplitude changes as might occur.

Effect of a Superimposed Direct Current Voltage

A 0.3 mf condenser was put in the lead to the test condenser and the section of the circuit between these two condensers was connected through a 17 megohm resistance and a micro-ammeter to the positive side of a high voltage direct current generator, the negative side of which was grounded. With this arrangement a direct current voltage could be superimposed on the high frequency voltage across the test condenser. The results of a few preliminary measurements may be stated briefly. When 900 volts measured at the generator, is applied the capacity of the evacuated test condenser increases by about 0.04 mmf. The effect is the same when the condenser contains air at a pressure large enough to prevent a discharge. When the pressure is reduced to 60 cm or less a discharge through the gas begins and under these conditions the capacity increase is definitely less than the value given above. Similar results are obtained with hydrogen and ammonia.

These results indicate that 900 volts or approximately 18,000 volts per cm produces a very small increase in the capacity of the condenser and no change in the dielectric constants of the gases used. The smaller effect observed when a discharge is passing through the gas is apparently not due to the slightly smaller voltage across the condenser in this case. It may be a genuine decrease in the dielectric constant produced by the discharge but is more probably a temperature effect. However, Seth[7] has recently reported an apparent decrease in the refractive index of air due to a discharge and a more careful investigation of the above effect might be worth while.

Department of Physics,
The Rice Institute,
April 28, 1928.

[7] J. B. Seth, Nature **120**, 880 (1927).

A SIMPLE RELATION BETWEEN THERMAL CONDUCTIVITY, SPECIFIC HEAT AND ABSOLUTE TEMPERATURE

By C. C. Bidwell

Abstract

A relation of the form $k/aC=K_1/T+K_2$, between thermal conductivity k, atomic heat (aC), and absolute temperature T, is shown to hold for zinc, sodium, lithium, copper, lead, aluminum and mercury. The possibility is indicated of an equation of this sort based on the assumption of a double mechanism of heat conduction—an atomic lattice along which energy is transmitted as elastic waves (Debye) and a structure of atoms (crystalline or amorphous), through which energy is transferred by impacts. The lattice and atomic contributions to the thermal conductivity may be obtained from the slopes and intercepts of the lines. The values at 0°C are as follows (lattice part being given first): lithium 0.150, 0.006; sodium 0.092, 0.169; zinc 0.084, 0.192; copper 0.920, 0.171; lead 0.018, 0.068; aluminum 0.127, 0.358; mercury 0.031, 0.033. The line for mercury suggests that the atomic part is at least approximately the conductivity in the liquid state. The single and poly-crystal zinc lines have the same intercept but different slopes indicating that the increased thermal conductivity of the single crystal specimen is in the elastic wave contribution.

A STUDY of recently obtained data on thermal conductivity and specific heat of lithium and sodium[1] and zinc and lead[2] over the temperature range -250°C to $+200$°C reveals a simple relation between these quantities, not hitherto specifically reported, namely the law

$$k/aC=K_1/T+K_2 \qquad (1)$$

where k is the thermal conductivity; (aC), the atomic heat; T, the absolute temperature and K_1 and K_2 constants. The values of k/aC when plotted against $1/T$ fit straight lines with remarkable precision. These plots are shown in Figure 1.* For lithium the law holds as far down as -200°C below which the rapid increase in k causes a deviation. For zinc a deviation becomes noticeable only below -225°C, while for sodium and lead there is no deviation as far as -240°C below which temperature we have no data. The plot shows also lines for copper, aluminum and mercury using data from the Landolt-Börnstein tables.

[1] Bidwell, Phys. Rev. **28**, 475 (1926).

[2] Lewis and Bidwell, Phys. Rev. **31**, 1111 (1928).

* The transformation at $+50°$ for lithium limits the upper temperatures since we have no data for the metal in the higher temperature modification. A transformation occurs in sodium between -40°C and 0°C; we have data above this region and the points are indicated. The following data for thermal conductivity of very pure zinc and lead, recently obtained by Bidwell and Lewis were used for this graph: For poly-crystal zinc: -250°C, 0.341; -200°C, 0.325; 100°C, 0.2975; 0°C, 0.273; $+100$°C, 0.255; $+200$°C, 0.2425; 300°C, 0.238. For single crystal zinc: -250°C, 0.382; -225°C, 0.373; -200°C, 0.3615; -100°C, 0.330; 0°C, 0.304; $+100$°C, 0.286; $+200$°C, 0.274. For lead: -250°C, 0.128; -200°C, 0.113; -100°C, 0.097; 0°C, 0.084; $+100$°C, 0.075. The lower range values for lead are higher than values reported by Meissner and Schott but agree with values found by Macchia.

The theory of thermal conduction is in a unsettled condition because of our lack of any certain knowledge of the mechanism involved. It has been suggested frequently that two distinct mechanisms are concerned in heat conduction in a metal; namely, a non-metallic part, i.e., transfer by atomic

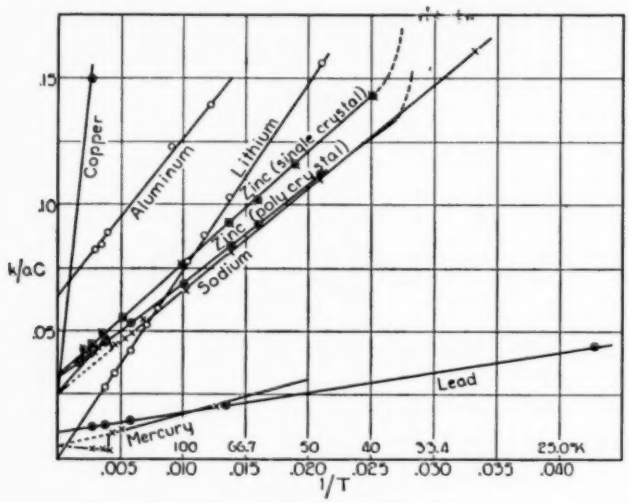

Fig. 1. Variation of k/aC with $1/T$.

collisions, and a metallic part, usually assumed as a transfer of heat by electrons. The equation above given likewise indicates a double mechanism and further shows that one part is a function of temperature, the other not.

Debye[3] has suggested the transfer of heat by elastic waves down a space lattice in which the energy of the wave is continually reabsorbed as heat, i.e., converted to atomic vibrations. His expression is

$$k_1 = \rho v' l' C_v / 4 \tag{2}$$

in which ρ is the density of the metal; C_v, the specific heat; v', the velocity of sound in the metal; and l', a dissipation factor, the distance the wave travels before its energy is reduced to $1/e$ of its value. It is reasonable to suppose that dissipation of the wave energy is greater at higher temperatures. Therefore, if we tentatively place $l' = A/T$, where A is a constant and divide the expression by aC (where a is the atomic weight) we have $k_1 = A\rho v'/4aT$, which corresponds to the first term of the experimental law, the term upon which the slopes of the lines depend. The increased slope of the single crystal zinc line is in agreement with this interpretatio· The factor A should presumably not be affected by the crystal size but the elastic constants and therefore v' should be so affected. Measurement of v' in the single and poly-crystal zinc rods should be of interest in this connection.

It is possible that the second term on the right, that is, the intercept, is the value of k/aC which has to do with the transport of heat by atomic

[3] Debye, Vorträge über die kinetische Theory der Materie und Electricität. Teubner, 1914.

collisions. According to the experimental law this term is independent of the temperature. The behavior of the mercury line suggests that this has approximately the same value as for the liquid metal. An expression for the liquid state which is independent of the temperature is readily obtained. Thus the heat transferred through unit area in unit times by collisions of individual atoms is $dH/dt=(1/3)vlNdE/dx$, where E is the kinetic energy of the atoms; N the number of atoms per unit volume; l, the mean free path; v, the root-mean-square velocity. We may write this as

$$\frac{dH}{dt}=\frac{1}{3}vl\rho\left[\frac{N}{\rho}\frac{dE}{dT}\right]\frac{dT}{dx}$$

in which $(N/\rho)(dE/dT)=C_v$, and ρ, the density. By definition $dH/dt=k_2(dT/dx)$, in which k_2 is the thermal conductivity. Therefore

$$k_2=\rho vlC_v/3 \tag{3}$$

There is some experimental evidence from other quarters that $l\propto 1/T^{1/2}$ or that $l\propto 1/v$. The expression thus is independent of the temperature.

Combining expressions (2) and (3) gives

$$k/aC_v=A\rho v'/4aT+\rho vl/3a \tag{4}$$

This equation is of the form required by the law. The second term on the right, however, applies to mobile atoms, whereas in the solid metals we are dealing with atoms spaced rigidly in a lattice.

The observed intercept for zinc is 0.032. Assuming the above term, we get l as of the order of 10^{-5} whereas the atomic spacing in the lattice is of the order 10^{-8}. Evidently then the term as derived for a liquid metal cannot be taken over, as it stands, for the solid. It should be possible, however, to obtain for the solid a term of this character.

Table I shows the values of $\rho v'/4a$, compared with the observed slopes, and also the computed values of A for the different metals. It is of interest to note that we have approximately the same value for A for lithium, sodium, zinc and copper, or that the slopes for these four metals are proportional to $\rho v'/4a$.

TABLE I. *Values of $\rho v'/4a$ and of A.*

Metal	$\rho v'/4a$*	Observed slope	A
Lithium	1910	7.5	0.00390
Sodium	1030	3.9	0.00378
Zinc (poly crystal)	994	3.8	0.00383
Zinc (single crysal)	—	4.4	—
Copper	12250	44.7	0.00365
Lead	1360	.8	0.00059
Aluminum	12700	6.3	0.00050
Mercury	7100	1.3	0.00018

* The values of the velocity of sound were taken from the Smithsonian tables for copper zinc and aluminum. For lithium, sodium and mercury, this was assumed as of the same order as for lead, which is about 1060. For these metals the value of 1000 was taken.

It is also of interest to observe on the basis of the equation and its interpretation as here given to what extent the thermal conduction is due to elastic waves and to what extent it is due to atomic collisions. Table II shows the value of $k_1 = K_1(aC/T)$ and $k_2 = K_2 aC$ for the various metals at 0°C.

TABLE II. *Elastic and non-elastic portions of thermal conductivity at 0°C.*

Metal	Elastic wave portion $k_1 = K_1\ aC/T$	Atomic portion $k_2 = K_2 aC$
Lithium	0.150	0.006
Sodium	0.092 (−10°C)	0.169
	0.124 (+10°C)	
Zinc (poly crystal)	0.084	0.192
Zinc (single crystal)	0.098	0.192
Aluminum	0.127	0.358
Copper	0.920	0.171
Lead	0.018	0.068
Mercury	0.0308 (solid-extrapolated)	0.0335

The theory suggests that the intercepts give a measure of the non-elastic or atomic portion of the thermal conductivity and that this portion is independent of the temperature if the atomic heat has become constant. The mercury data indicate that this is approximately at least the thermal conductivity for the metal in the liquid state. (The slight negative slope of the liquid mercury line may be due to inaccurate data on k and C.) The line for single-crystal zinc shows a greater slope than the line for poly-crystal zinc but exactly the same intercept. The increased thermal conductivity, therefore, is entirely in the elastic wave portion as we would expect on the theory presented. Likewise the change in the sodium line just below 0°C indicates that the increased conductivity is entirely in the elastic wave portion since the slope is increased while the intercept remains the same.

We expect for the metals k_1 to be much larger than k_2 and this is borne out for lithium and copper but sodium, zinc and lead curiously enough show k_1 smaller than k_2, while mercury shows about an equal division. The difference between a metal and a non-metal is usually ascribed to the presence of mobile electrons in the metal. It is not clear just what part the electrons play in thermal conduction. Possibly we may think of an electron lattice upon which the atoms act as drags. This would account for the rapid attenuation of the wave while also explaining the high thermal conductivity of metals. We would have to assume the absence of such a mobile electron lattice in non-metals. Data on other metals are being obtained to test the equation and theory further, particularly, for the liquid state.

LEHIGH UNIVERSITY,
March 25, 1928.

BOOK REVIEWS

Vorlesungen über Elektrizität. A. EICHENWALD. Pp. 664, 640 figs. Julius Springer, Berlin, 1928. Price R.M. 36 unbound.

The pictures are the most striking part of the book. Practically every subject of importance is illustrated by a photograph or a diagram. The pictures are very clear and should be of great pedagogical assistance. The presentation of the subject is elementary and should be suitable for a beginner. The reader is gradually led into the more advanced parts. The object is that of presenting physical facts rather than training the student in solving problems. The fundamental results of mathematical electricity and magnetism are not forgotten. However, they are presented in the language of Faraday rather than that of Maxwell or Lorentz. In addition to phenomena discussed in classical texts, attention is given to radioactivity, x-rays, atomic structure, nuclear disintegration, and the periodic table. Quantum theory is touched upon. The experiments of Einstein and de Haas, Tolman and Stewart, and Stern and Gerlach are described and their fundamental nature is brought out. A sketch of radio developments is given. The last 19 pages of the book are devoted to a mathematical presentation of Maxwell's theory including an introduction into vector-analysis.

The elementary portions of the book will be probably found very useful. The presentation of the more advanced parts, however, is decidedly incomplete. It is questionable whether the somewhat antiquated presentation of quantum theory along the original Bohr lines should have been included. There are so many books and papers of both a technical as well as popular nature dealing with this subject. The same applies to radio. It is very refreshing, however, to see so many fundamental experiments mentioned clearly in an elementary text.

G. BREIT

Lehrbuch der Elektrodynamik. J. FRENKEL. Zweiter Band. Makroskopische Elektrodynamik der Materiellen Körper. Pp. 505, 50 figs. Julius Springer, Berlin, 1928. Price R.M. 45.00 unbound.

This volume has a scope comparable to Abraham-Föppl's second volume of the Theorie der Elektrizität. Being a modern book, it pays much more attention to relativity and takes it as a guiding principle in many parts. The center of gravity is put into the first part where the macro equations are derived. The process of passing from the micro to the macro equations is very clearly presented. In order to emphasize the difference in the definitions of the usual E and H, the author reverses the customary notation for H and B. Effects of quadrupoles are worked out in the same section and at every point generalizations to moving bodies are made. Maxwell's stresses are treated in great detail. One can be in great sympathy with this first portion of the book.

From there on we find a rather miscellaneous collection of topics such as Langevin's law, electrical oscillations on wires, propagation of radio waves, conduction in metals, propagation of waves in anisotropic media, etc. None of these is treated exhaustively, and the experimental data are usually mentioned only in a general way. In these sections the book is comparable to that of Livens. The methods and the reasoning used are usually clearer with Frenkel.

The detail and thoroughness of the first part seem out of proportion to the superficial treatment in the later portions. An American student with sufficient training to study the beginning of the book would find the treatment of condenser discharges unnecessary. The treatment of radio waves is hardly more than a mathematical exercise in its importance to the phenomena actually taking place. A mathematical appendix (43 pages) presents curvilinear coordinates and the standard equations of mathematical physics.

G. BREIT

Les bases de la geométrie et de la physique. L'invariance de l'éspace euclidien. CLEMENT LAURÈS. Pp. 125, 21 figs. Blanchard, Paris, 1928.

On p. 5 of this pretentious little book of 125 pages we read: "The human mind is sick. It bears many poisoned fruit from the tree of science. The time has come to eliminate . . . . all the poison. . . . . Don't we see . . . . another stupidity, the elder daughter of the first (Non-Euclidean geometry)? I mean the theory of relativity. . . . ."

P. 11 brings this: "The postulate of Euclide can be proved. The fact that it has not been done till now only proves the weakness of the human mind."

P. 48: "There exist in fact in his (Lobachevsky's) space similar triangles. The proof of this is given by the existence of an infinity of isoceles triangles with the same angle at the vertex."—The same reasoning would prove the existence of similar (not equal) triangles on a sphere.

P. 106: "Only the anomaly in the motion of Mercury's perihelion appeared inexplicable. . . . . Now, Newton's theory explains it very well. But it is necessary for that purpose to cease assuming that the Sun is immovable and to consider it . . . . as a body in motion around the common center of gravity . . . . rotating about this point during the time which the light emitted by it takes to reach the planet. The algorithm of the tensor calculus is nothing but a method—a little complicated method—of taking this motion into account."

P. 120. "The distinction between independent motions and bound motions (mouvements liés) is fundamental and using it one can conveniently explain the experiment of Michelson and Morley." But the explanation is not given.

To be fair to the author it is necessary to say that the book is not so uniformly nonsensical as might appear from these quotations, that it contains sensible and even interesting passages, and possibly ideas. But the main trend of thought and achievements probably are adequately characterized by the quotations. G. Y. RAINICH

Das Experiment, Sein Wesen und Seine Geschichte. HUGO DINGLER. Pp. 263. Ernst Reinhardt, Munich, 1928. Price, R.M. 8.80 unbound.

This book, whose author is professor of philosophy at the University of Munich, will doubtless make its chief appeal to an audience with philosophical training and interests, but there are nevertheless many features of the book which the physicist who is interested in fundamental matters will find suggestive and of value. Especially illuminating is the section on the history of experiment, in which it is shown how long and arduous a mental preparation, in modifying commonly accepted forms of thought, was necessary before we were ready for the experimental method.

It is the main thesis of the book that the essence of experiment consists in discovering in experience certain recurring combinations or "forms," which are recognizable, and which we can reproduce. The forms which we choose as fundamental are largely in our control through the definitions which we give them, so that the appearance of nature is also largely in our control. Thus Dingler presents as one of his main results the conclusion that space must be Euclidean. "I am able here to carry through the exact proof that non-Euclidean geometry is impossible in practice, and that no experiment can ever give a direct quantitative ('messenden') proof of the existence of a non-Euclidean geometry." (page 37). The proof of this proposition follows from the fundamental definition of a plane, which is defined as a surface exactly the same on both sides. This definition is shown to lead to the same result as the practical procedure adopted by instrument makers for making a test plane by working three surfaces together until any two of them placed together are in contact at all points. Dingler stresses the importance of thus referring the definition to actual manual procedure.

With this effort of Dingler to express his definitions in terms of actual procedure I am heartily in sympathy, and it is indeed very close to what I have called the "operational" point of view. But not only must the definitions be operational, but the way in which the fundamental operations are defined is equally important. What assurance have we that a surface exists which is the same on both sides, or that the instrument maker's procedure for fitting three test planes will ever lead to a final or a unique result when the accuracy of measurement is indefinitely increased? If one questions an instrument maker about his procedure, he will find it more of an art than a science, and any rules of procedure which he is able to definitely formulate are in

terms of the Euclidean geometry which we are trying to establish. It seems to me fairly obvious that the fundamental operations ought not to be defined in terms of their results; even the patent office does not allow a description of an invention in terms of its function. The fundamental operations must be directly defined in such terms that they may be definitely and uniquely carried out. Dingler, it seems to me, has defined his operations in terms of results, so that it is just as questionable whether his conclusions apply to reality as, for example, whether there is in reality the prototype of Newton's absolute time with its absolute simultaneity.

P. W. BRIDGMAN

Mathematical and Physical Papers, 1903–1913. BENJAMIN OSGOOD PEIRCE. Pp. 444. Harvard University Press, Cambridge, Mass. 1926. Price $5.00.

This handsome volume contains most of the papers published by the late Professor B. O. Peirce in the last ten years of his life. With his usual modesty he had taken no pains to give them wide publicity. This collection has been made by some of his colleagues to meet the demands of many who wished to consult these papers, and to serve as a memorial of a man respected and loved by every one who knew him.

There are a few papers in this volume on pure mathematics, of the type that used to be applied in mathematical physics, but the greater number of them deal with experimental problems in magnetism. The first paper is concerned with the properties of permanent magnets made of chilled cast iron for use in d'Arsonval galvanometers. The direction given to the author's thought by his work on this small problem led him on to elaborate studies of the behavior of the core of an electromagnet when a current was being set up in its coils, and of the magnetic properties of various types of iron and steel. The treatment of these and similar problems exhibit the author's extensive knowledge, his accurate and sound judgment, and his unwearied industry. The collection is a worthy memorial to a great man.

W. F. MAGIE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE POMONA MEETING, JUNE 15, 1928

The 152nd regular meeting of the American Physical Society was held in Pomona, California, at Pomona College, in affiliation with the Pacific Division of the American Association for the Advancement of Science. The meeting of the American Physical Society was held Friday, June 15th, the morning session being a joint session with the Astronomical Society of the Pacific. The program consisted of forty-two papers, eleven of which—Nos. 4, 25, 29, 33, 34, 36, 37, 38, 40, 41, and 42—were read by title. Abstracts of these papers are given in the following pages. An Author Index will be found at the end.

S. J. BARNETT
Acting Local Secretary for the Pacific Coast

ABSTRACTS

1. The spectrum of sulphur S II. S. B. INGRAM, California Institute of Technology.—The sulphur spectrum in the extreme ultra-violet was photographed with a vacuum spectrograph and a hot-spark source. Above 2000A a seven meter concave grating was used, the spectrum being obtained from a discharge tube in H_2S gas. By varying the conditions of excitation the spectrum of S II could be separated from the spectra of higher stages of ionization. One hundred and eighty-three lines have been classified and the following terms identified: s^2p^3, ^4S $^2(PD)$; sp^4, ^4P, ^2P; $s^2p^2 \cdot 4s$, ^4P, $^2(PD)$; $s^2p^2 \cdot 5s$, ^4P, ^2P; $s^2p^2 \cdot 4p$, $^4(SPD)$, $^2(PD, PDF)$; $s^2p^2 \cdot 3d$, ^4F, $^2(PDF)$; $s^2p^2 \cdot 4d$, $^4(PDF)$, $^2(DF, G)$. The low ^4S term has a value of 188824.5 cm^{-1} corresponding to an ionization potential of 23.3 ± 0.1 volts for the S II ion.

2. On the spectra of doubly ionized vanadium, V III, and triply ionized chromium, Cr IV. H. E. WHITE, Cornell University.—The neutral atoms of vanadium and chromium contain five valence electrons, ($3d^34s^2$), and six valence electrons, ($3d^54s$), respectively. The removal of two electrons ($4s^2$) from vanadium and three electrons ($3d^24s$) from chromium gives two iso-electronic systems, V III and Cr IV, the lowest energy levels of which are given by the remaining valence electrons $3d^2$. From the relations known as the irregular doublet law applied to multiplets, and a Moseley Diagram for multiple levels, along with the arc and spark spectrum of scandium and titanium respectively, doublet and quartet terms of the three electron configurations $3d^3$, $3d^24s$, and $3d^24p$ have been determined for V III, and Cr IV. From Sc I and Ti II a linear extrapolation of the radiated lines arising from the electron transition $3d^24p$ to $3d^24s$ was sufficient to locate the corresponding lines for V III around 2300A, and for Cr IV around 1800A. The terms thus determined for $3d^24p$ combine with the lowest energy levels in the spectrum, $3d^3$, giving very strong lines in the region, 1100A for V III, and 600A for Cr IV. With this determination of the lowest energy level of $3d^3$ the ionization potentials for V III and Cr IV are computed at 30 volts and 52 volts respectively.

3. Doublets and quartets of doubly ionized silver, Ag III. R. C. GIBBS AND H. E. WHITE, Cornell University.—For a sequence of iso-electronic systems starting with any element in the periodic table, if the energy levels representing any of the possible electron configurations be

plotted on a Moseley type of diagram, the lines connecting corresponding terms of each successive element will be very nearly straight lines. Furthermore it is found that the radiated frequencies resulting from those electron transitions involving no change in total quantum number (which in some cases involve at least a hundred radiated lines) are displaced to higher and higher frequencies by very nearly a constant value. Applying these relations to the known arc spectrum of rhodium, Rh I, and the first spark spectrum of palladium, Pd II, some of the doublet and quartet terms arising from the electron configurations $4d^9$, $4d^85s$, and $4d^85p$ of the second spark spectrum of silver have been determined. The transitions from $4d^85p$ into $4d^9(^2D_{2,3})$ makes it possible to determine the term value of the lowest energy level in the spectrum from which the ionization potential of Ag III is calculated to be about 34 volts. The large term separations which are characteristic of the heavier elements in the periodic table are shown by the $^2D_3-^2D_2(4d^9)$ separations, $\Delta\nu=2348$, $\Delta\nu=3538$, and $\Delta\nu=4607$ for Rh I, Pd II, and Ag III respectively.

4. Structure of praseodymium lines. ARTHUR S. KING, Mount Wilson Observatory.—The complex structure of praseodymium lines, mentioned in a former report, has been examined in more detail by means of high dispersion. Of the stronger lines from λ3100 to λ6800, nearly 400 have been listed as complex. The largest proportion is among the singly ionized lines in the blue and violet but many examples are found also in the neutral spectrum. The complexity varies from double lines to those of six components. The prevailing types are wide and narrow patterns with components of equal intensity, and wide patterns in which there is a progressive increase in resolution of components from violet to red or vice versa. The maximum interval in a six-component line of the latter type is about 0.06A, the intervals decreasing to 0.03A. Lines compared in furnace, arc and spark spectra appear to retain their structures unchanged. Recurring lines of each type in a given region indicate the presence of multiplets, and as many of these lines are of low atomic level, their similarities should aid in the analysis of the spectrum, and give additional evidence on the connection of such structure with the metastable states.

5. An optical oscillograph. SINCLAIR SMITH, Mount Wilson Observatory.—A beam of light after passing through a nicol prism, a quartz plate (perpendicular to the axis), a CS_2 cell, and a second nicol, is photographed with a rotating mirror spectrograph. The current to be studied is carried by a solenoid which surrounds the CS_2 cell. The first nicol renders the light plane polarized, the quartz plate rotates the plane of polarization according to the law $\theta=A+B/\lambda^2$, and the CS_2 cell adds to or subtracts from the rotation, depending on the current through the solenoid. The second nicol removes all wave-lengths from the beam which have suffered a rotation of $n\pi$ where n is an integer. Thus, if the light coming through the second nicol is viewed through a spectroscope, the spectrum is seen to consist of a series of bright and dark bands, the position of the dark bands depending on the current through the solenoid. If the light is photographed with a rotating mirror spectrograph while a non-uniform current is flowing through the solenoid, the fluctuations of the current are reproduced on the film. Professor Bedell has informed the author that a similar scheme was suggested by Crehore in 1894.

6. Effect of pressure and current density on the spectrum of Helium. A. C. HODGES, California Institute of Technology.—A study has been made of the intensities of the various lines of the spectrum of neutral helium, with the particular view of obtaining regularities in the variation of relative intensities with changes of current density and pressure. The method used was a modification of that developed by Ornstein at Utrecht, the modification consisting of a direct comparison of intensities of the helium lines with the same wave-lengths in the continuous spectrum from a standardized tungsten filament. A study has been made of the lines 5876, 5016, 4922, 4713, 4472, 4387, 4143, 3964, 3889, 3819, at pressures of 27, 9, and 3 mm, and currents of 65, 20, and 4 milliamperes in a capillary discharge. The results show an increase of the relative intensities of the higher members of the various series with a decrease of pressure or current density.

7. Locus of secondary image for two plane mirrors independently variable about parallel axes situated in the two respective planes. L. E. DODD. University of California at Los Angeles.—This problem is one in geometrical optics. Given two plane mirrors independently variable about parallel axes located one in each plane; required, the locus of the secondary image (in "second" mirror) of object point O. Pass a plane through O perpendicular to both mirror axes. A_0 and A are points where axes of first and second mirrors respectively cut this plane. A_0 is at left of A, both on the x axis, and O above both. Draw AO and OA_0, take A_0 as the origin, denote the distance A_0A by d, AO by r, OA_0 by D, and the angles A_0AO, AOA_0 by μ and ν. Draw a straight line through A, one through A_0, making arbitrary angles ξ and η with the x-axis, representing first and second mirrors. (Reflecting surface of the first is upward, that of second downward. Observer's position is below the x-axis. The question of cutting away of mirror planes for practical cases can be treated as a separate problem.) Draw OPO' perpendicular to M_1; $O'QO''$ perpendicular to M_2. O' is the image of O in M_1, O'' the image of O' in M_2. Required, A_0O'' $(=\rho)$ and angle AA_0O'' $(=\phi)$, coordinates of O'', in terms of the parameters d, r, D, and variables ξ, η. The solution is $\rho^2=D^2+2r\sin\alpha\,[2r\sin\alpha+2D\sin(\nu-\alpha)]$, where $\alpha=(\pi-\xi-\mu)$, $\mu=\cos^{-1}[(r^2+d^2-D^2)/2rd]$, $\nu=\cos^{-1}[(r^2-d^2+D^2)/2rD]$, and $\phi=\alpha+2\eta-\xi-\cos^{-1}[(\rho^2+r^2-d^2)/2\rho r]$.

8. An extension of the Cd I-like iso-electronic sequence to Sb IV. ALICE M. VIEWEG AND R. C. GIBBS, Cornell University.—In its neutral unexcited condition the antimony atom contains five valence electrons ($5s^2\,5p^3$). On removing three of these electrons antimony takes its place as the fourth element in the sequence of iso-electronic systems starting with cadmium; Cd I, In II, Sn III, Sb IV. By means of an almost linear extrapolation from classified lines emitted in the case of cadmium, indium and tin, in transitions from electronic configuration $5s6s$ to configuration $5s5p$, and $5s5d$ to $5s5p$, it has been possible to locate some of the corresponding lines in the spectrum of Sb IV. These lines are in the region 800–950A. We hope soon to identify more of the lines in the third spark spectrum of antimony and to extend this investigation into the spectrum of Te V.

9. The first spark spectrum of arsenic, As II. C. W. GARTLEIN, Cornell University.—The spark spectrum of arsenic was photographed below 2300A in a vacuum spectrograph using varying amounts of inductance in series with the spark. The As II lines were present in the spark even with large amounts of inductance but the lines from higher states, though present with no inductance, decreased in intensity as the amount of inductance was increased. It was also observed that the spectrum of As II was characterized by "long lines" due to glowing arsenic vapor that extended above and below the short vertical spark gap. About 75 lines have been arranged into a term scheme. All the terms of the lowest configuration, $(4p)^2$, and of the $4p5s$ configuration have been identified as well as some terms from the $4p4d$ configuration. Part of the terms due to the $4p5p$ configuration have been identified by lines in the visible spectrum due to transitions into the levels of the $4p5s$ configuration. The most prominent lines of the spectrum were identified by analogy with that of Ge I.

10. An erythema meter. ROBERT C. BURT, R. C. Burt Laboratory, Pasadena.—Erythema (sunburn) being one of the most definite and quickest observable biological reactions to ultra-violet, it is often taken as a criterion of the ultra-violet present. Besides the variable of skin, complexion, etc., little seems to be known as to the form of the time integral. An instrument is described which plots on the skin the time-intensity curve from which this integral may be determined. Observations are also taken of the growth and disappearance of erythema. It may be remarked that the erythema constant for an individual may be determined to about 10%.

11. On negative values of θ in the law of paramagnetism $K(T-\theta)=C$. LARS A. WELO. The Rockefeller Institute for Medical Research, New York.—Six iron salts of the type $[Fe_3(CH_3COO)_6(OH)_2]Cl$ obey the law $K(T-\theta)=C$ with normal values of $C=4.2$, but values of θ range from -553 to -695. Ten chromium salts of the same type give normal values of

$C=1.9$ with values of θ ranging from -89 to -116. CH_3COO may be replaced by CHOO, CH_3CH_2COO, C_6H_5COO, etc. An interpretation along classical lines is possible if we consider the organic groups as electric dipoles and adopt Debye's suggestion (*Handbuch der Radiologie*, vol. 6, p. 704) that the metallic ions have permanent electric moments as well as magnetic moments. The complex ion is then a semi-rigid structure in which the orientations of the metallic ions are electrostatically controlled by the organic groups. (For example: a triangular model, each side consisting of the chain $CH_3COO \cdot Fe \cdot CH_3COO$). In such a structure, the control which resists orientation by a magnetic field is, at every instant, equal to the control which resists disorganization by temperature agitation, and the ratio of the magnetization (or susceptibility) to its temperature coefficient should be a constant. But this is precisely the law $K(T-\theta)=C$, since in it the temperature coefficient is the quantity $-1/(T-\theta)$.

12. Measurements of thermoluminescence of glass exposed to light. R. E. NYSWANDER and B. E. COHN, University of Denver.—Glass turned violet in color due to long exposure to sunlight is thermoluminescent when heated to temperatures above 100°C. Thermoluminescence was also observed in some samples free from color, while others showed no luminescence. Effects similar to those for sunlight were also observed from glasses exposed to the carbon arc and in some cases for exposures of only a few minutes. Special glasses were made from a chemically pure zinc borate glass to which was added a trace of one of the following metals: barium, calcium, strontium, magnesium, manganese, aluminum, nickel, cobalt, chromium, silver cerium and thorium. Each of the above was exposed to sunlight and tested for thermoluminescence, the most intensely luminescent being thorium, cerium, silver, chromium cobalt and manganese. The following observations and curves were determined: growth of luminescence with time of exposure, both for sunlight and the carbon arc: effect of absorption of exciting rays due to thickness of glass: effect of concentration of solute: thermoluminescence as dependent upon temperature at excitation: total quantity of light emitted: and decay of thermoluminescence. All light measurements were quantitative and were made with a polarization photometer (Nyswander and Lind, J.O.S.A. & R.S.I., Vol. 13, No. 6, p. 551). The specimens were heated in an electric furnace.

13. Hall effect in bar of electrolytic iron. EMERSON M. PUGH, Unrversity of Pittsburgh.—The Hall effect was measured in a bar of electrolytic iron in contrast to the usual method of measuring it in thin sheets of the material. Direct measurements were taken at the same time of the magnetic induction B and of the Hall e.m.f. $-E$ The $E-B$ curve is shown to be a straight line up to $B \doteq 12{,}000$ lines/cm² where its slope starts to decrease. A curve of magnetizing current vs. B is seen to break away from a straight line at about the same value of B. Measurements taken at points on a "hysteresis loop" indicate that E is also proportional to B where B is due only to residual magnetism. The Hall coefficient for this bar is found to be 20 percent lower than that found by A. W. Smith for electrolytic iron.

14. Instantaneous line intensities in the alternating current arc. BRIAN O'BRIEN AND E. DICKERMAN O'BRIEN, Research Laboratories, Buffalo Tuberculosis Association, Perrysburg, N. Y.—A carbon arc containing Na and Mg salts was operated from an inverted rotary converter, to the shaft of which was attached a sector shutter so arranged that the arc could be observed continuously at any part of the alternating current wave. A contact device attached to the shaft provided for measurement of the instantaneous current through and voltage across the arc. Line intensities were determined with a small quartz spectrograph by a photographic method. Variations of intensity for the prominent lines of Na and Mg were determined throughout the alternating current cycle. Ratio of intensities of the Mg lines at 2795A, 2803A, and 2852A gave a measure of the relative ionization.

15. Gas phenomena and contact behavior in a vacuum switch. F. C. LINDVALL, California Institute of Technology.—A conditioned vacuum switch opens a circuit with a small, momentary arc. A definite rise in gas pressure within the switch is observed to follow continued switch operation. The rate at which gas is evolved is found to depend both on the val· ·f the

interrupted current and on the circuit voltage, increasing either for increasing current or for in creasing voltage. Further, definite evidence of "getter-action" in the switch was obtained. Thus the resultant gas pressure was found to be due to that part of the evolved gas not taken up by getter-action; and a limiting equilibrium case was found in which the gas evolution and the clean-up balance each other to give a constant operating pressure for indefinitely continued switch operation. Moreover, these tests gave limiting values of gas pressure for satisfactory operation. In addition, the investigations included rupture of currents that gave excessively high contact current densities, and demonstrated that breaker operation is possible even with severe heating of the contacts. Repeated tests gave similar results for three contact metals copper, aluminum, and tungsten.

16. Measurement of arc voltage across opening switch contacts. HUGH HAMILTON, California Institute of Technology.—The measurement of arc voltage presents the unique problem of determining a small voltage of the order of 20 volts, existant for a fraction of a second which is immediately followed in the case of a circuit breaker by full line potential. The apparatus developed for this purpose consists of a high voltage kenotron in series with a 140 volt battery and an oscillograph. This circuit was connected across the switch contacts. Low voltages in the switch were thereby reproduced on an oscillogram, but high currents due to high voltages were suppressed by the saturation of the kenotron. The rated current of the oscillograph was therefore never exceeded. The results obtained with the vacuum switch establish two facts. The arc voltage proper is low and of the order of 10 to 25 volts. The arc voltage is independent of the current except for low current values. The cathode spot theory explains the performance of the switch and seemingly is in accordance with all the observed phenomena. For currents of the order of 5 amperes the arc voltage is high apparently due to the disappearance of the cathode spot. Sufficient work with these values has not yet been done to completely describe this action. Comparison of arc energy in the vacuum switch with that of the oil switch under the same circuit conditions showed that the oil switch energy is of the order of 100 times greater. The arc voltage in the oil circuit breaker is 8 to 10 times that of the vacuum switch.

17. Single crystals of metals formed in magnetic fields. A. GOETZ, California Institute of Technology.—The author has developed a method for producing single crystals of metals (Bi, Sn) in which the crystallization occurs in a strong magnetic field. If desired, half of the crystal can be grown in the field and the other half without the field. In this way, crystals are obtained which show no visible crystallographic discontinuity, but which show a marked discontinuity in electrical properties. The two halves exhibit a thermoelectric potential at their junction, and also have different changes of electrical resistance in a magnetic field.

18. A new high voltage x-ray tube. C. C. LAURITSEN AND R. D. BENNETT, California Institute of Technology.—This paper describes the construction of a tube by means of which it is hoped to extend the investigation of radiation from the now known x-ray region well into the region of gamma rays. The tube is designed for operation in connection with a 1,000 K.V.A. transformer-set capable of producing peak voltages up to 1,500,000 volts. The tube consists of glass cylinders 12×28 inches, placed end to end and thoroughly shielded inside against bombardment. The source of electrons consists at present of the rounded end of a tungsten rod 8 mm in diameter which can be retracted into the cathode sheath, thus enabling control of the field to which the point is exposed, and thereby of the electron emission The design also permits the use of a hot cathode if this should be found desirable. So far stable operation has been obtained well above half a million volts, and for short periods of time, about one million volts have been applied. The rectified current is from 5 to 25 milliamperes. Radiation can be observed by means of a fluoroscope at distances of more than a hundred feet, but so far no attempt has been made to analyse it.

19. Lagrangian functions which determine a symmetrical tensor by Schroedinger's rule, HERVEY C. HICKS, California Institute of Technology.—The choice of a Lagrangian function to be used in a variational principle may be limited by the condition that the tensor derived

from it by Schroedinger's rule shall be symmetrical. To meet this condition the function must satisfy a certain set of partial differential equations. Particular and general solutions of these equations are found in various cases—according as the function is restricted to depend (A) only on the components of a vector, (B) only on their first derivatives, or (C) on both; and according to the number of dimensions of the vector. Methods of obtaining such solutions, and of proving their independence or of finding the relations between them, are discussed.

20. Some problems in the steady motion of viscous, incompressible fluids; with particular reference to a variation principle. CLARK B. MILLIKAN, California Institute of Technology.—The question of the possible existence of steady motion in the general case of the flow of a viscous incompressible fluid, is investigated from the standpoint of a minimum or variation principle. It is shown that except for certain "exceptional cases" no Lagrangian Function exists, containing only the velocity components and their first order space derivatives, and from which the equations of motion may be deduced through the application of a variation principle. It is concluded that it is very probable that no steady state of motion exists for such a fluid, except in the "exceptional cases" defined in the paper. All the known examples of steady motion are shown to belong to this class of "exceptional cases"; and the Lagrangian Function for each of them is deduced and given explicitly. It is found that all of these Lagrangian Functions contain the same quantities and are in fact of the same general form.

21. Effect of toluene on the photoelectric behavior of mercury. DUANE ROLLER, California Institute of Technology.—When toluene vapor was introduced into an evacuated photoelectric cell containing freshly distilled liquid mercury, the sensitivity increased and the threshold shifted toward the red. The effect was immediate and its magnitude depended on the amount of vapor introduced. When vapor at 75 mm. pressure was held in the cell for one hour, the threshold shifted 100A. Upon connecting the cell to liquid air trap and pumps, the mercury surface not being disturbed in the meantime, the threshold gradually returned to the value for pure mercury. The time of return varied between 5 minutes and 46 hours, depending on the amount of vapor introduced and on the length of time it was held in the cell. The effects of xylene on both solid and liquid mercury are being investigated.

22. The direction of ejection of x-ray electrons. J. A. VAN DEN AKKER AND E. C. WATSON California Institute of Technology.—In a previous paper (Proc. Nat. Acad. 13, 659 (1927)) we have shown that the most probable direction of ejection of x-ray electrons depends to only a slight extent, if at all, upon the energy of binding of the electrons ejected. Evidence is now brought forward to show that this most probable direction of ejection is different for the electrons from the various M levels of a given atom. The same is true for electrons from the various L levels. This cannot be due solely to differences in the binding energies of these levels as these differences are small compared to the energy of the ejecting quantum (electrons ejected by the $K\alpha$ rays of molybdenum from exceedingly thin films of gold, silver, and tungsten have been studied). We conclude therefore that the direction of ejection depends upon the "shape" rather than the energy of the level from which the electron is ejected.

23. On the concentration of space charge in the vicinity of an insulating surface. BENEDICT CASSEN, California Institute of Technology.—The purpose of this investigation is the determination of the order of magnitude of the highest densities of space charge experimentally producible in the immediate vicinity of an insulating surface. Given a plane infinite emitting cathode and a plane parallel anode covered with a thin layer of insulating material of specific inductive capacity κ and thickness t, the following formula is derived for the density ρ_0 of charge, in e.s.u., at the surface of the insulating film when the anode is V volts positive with respect to the emitting surface,

$$\rho_0 = (9\times 10^4/4\pi)(\kappa VkT/ted)^2$$

where d is the distance between the emitting and insulating surfaces, e is the electronic charge in e.s.u., k is Boltzmann's constant and T is the absolute temperature. Some experimental work is described in which the maximum value of V that several insulating films could withstand before breaking down, is determined. For an ordinary aluminum oxide film this was found

to be about 27 volts. This indicates that the highest particle density of electrons obtainable in this way is of the order of 10^{12} to 10^{14} electrons per cm^3. This is very far from the degeneration concentrations so that the treatment of the problem by classical statistical considerations is justified.

24. Heats of linkage of C-H bonds from vibration spectra. JOSEPH W. ELLIS. University of California at Los Angeles.—Frequencies of bands at 3.28, 1.68, 1.145, 0.874, 0.713, 0.608, 0.532 and 0.476μ in the absorption spectrum of liquid benzene are expressible by a formula for a quantized anharmonic vibrator: $\nu^n = 3090n - 58n^2$. These yield mechanical frequencies: $\omega^n = 3090 - 116n$. These frequencies are assumed to originate in oscillations of a hydrogen atom with respect to the phenyl radical, the restoring force residing in the C-H bond. Using the method adopted by Birge and Sponer in measuring the heats of dissociation of non-polar, diatomic, gaseous molecules, the heat of linkage of a benzene C-H bond is here determined as 117,000 cal/mol. Corresponding values for hexane, cyclohexane and chloroform yield 97,000, 94,000 and 108,000 cal/mol respectively. The heat of linkage determined thermochemically for a methane C-H bond is 92,500 cal/mol. It is believed that this value checks with that determined optically for its homologue, hexane, within the limits of determination of the two values. The variations among the different compounds exceed experimental errors, and are believed to disprove the chemist's assumption of the equivalence of C-H bonds for all types of hydrocarbons. Wherever the resolving power of the spectroscope was sufficient to reveal it, the bands of hexane and cyclohexane (and other molecules not considered here) were observed double. This doubleness is here credited to an inequivalence of the four carbon valencies.

25. On the thermodynamical equilibrium of the universe. F. ZWICKY, California Institute of Technology.—The investigations on the equilibrium between radiation and matter by Stern and others, and the striking results on transformation of nuclei obtained by Millikan and Cameron make it desirable to work out the postulate of the thermodynamical equilibrium of the universe. The writer adopts the statistical method developed for chemical reactions by Ehrenfest and Trkal. Atoms, dust particles and stars are considered as molecules. For the typical reaction ν atoms $(m) \rightleftarrows$ star the equilibrium constant proves to be essentially $n_a^{\nu}/n_s = \rho^{-\epsilon/kt}$ where $E \cong fM^2/R$ is the gravitational potential energy of the star. (For the sun it is $E \cong 3.8 \times 10^{48}$ ergs, $\nu = 2 \times 10^{55}$ with $\bar{m} = 50$). This accounts readily for the abundance of the stars and the tremendously small vapor pressure of the atoms, also for the high temperature of the stars in spite of the low average temperature of the universe; for the formation of highly probable reaction products always involves excessively high kinetic energies for the individuals in the transition state. The complete picture of the equilibrium of the universe appears to involve on the one hand the transformation of matter into radiation (mainly in the stars) and the inverse process radiation $\rightarrow$ protons + electrons $\rightarrow$ higher nuclei going on throughout the spaces, conforming to Millikan's interpretation for the origin of the penetrating radiation.

26. The insulation of vibration. VERN O. KNUDSEN, University of California at Los Angeles.—The adaptation of electric circuit theory to mechanical systems is shown to offer a cogent means of investigating problems in the insulation of vibration. For example, it can be shown that any object of mass m separated by means of an elastic support or suspension from a framework (as a table or a building) which is vibrating with a frequency $\omega/2\pi$ and an amplitude a_1, is set into sympathetic vibration of amplitude $a_2 = a_1(r^2 + 1/\omega^2c^2)^{1/2}/[r^2 + (\omega m - 1/\omega c)^2]^{1/2}$, where c is the compliance (displacement per unit force) and r the resistance (mechanical ohms) of the elastic support or suspension. This equation has been verified experimentally for suspended systems having different values of m, c and r, for values of ω between 0 and 150. The factor r in most suspended systems using spiral springs or rubber bands is not significant except for high frequency vibrations. It is, however, very significant for systems where the "insulating pad" is cork or hairfelt or other materials having high internal damping. For $\omega^2 < 2/mc$ the "insulating" support or suspension gives an actual amplification of the vibration, the maximum occurring at the resonant frequency. Data are given for a typical suspended system. The usefulness of the theory is indicated by showing its application to a number of practical problems, as the prevention of vibration in apparatus and buildings.

27. An experimental method of measuring the electrostatic induction of the sun's negative charge upon the earth. FERNANDO SANFORD.—A quadrant electrometer has one diagonal pair of quadrants removed and the other pair connected together and to the metallic suspension of the needle. This system is insulated upon amber supports inside a closed metal case which is connected to the inside of a grounded wire cage and to the city water system. After being discharged to earth and allowed to stand insulated and doubly screened from outside induction the needle goes through a double oscillation every 24 hours, the range of which is more than the deflection which is produced by charging the insulated system to 150 volts. Two electrometers of different pattern and of different sensitivities give simultaneous corresponding deflections. Electric charges are measured from the earth taken as zero. An uncharged insulated body would become charged if the magnitude or the distribution of the earth's charge should change. The night side of the earth remains electronegative to the day side, hence the insulated system is positively charged at night and negatively charged by day. The potential difference of these charges is more than 150 volts.

28. The thermionic and photoelectric emission from Pt and Pd. LEE A. DUBRIDGE, National Research Fellow, California Institute of Technology.—Preliminary results of more precise measurements of the thermionic emission from outgassed platinum over a wide range of temperature confirm those previously announced that for the clean surface $b = 74{,}000°K$ and $A = 14{,}000$ amp/cm^2 deg^2, approximately. The emission currents are very small and are measured with a Compton electrometer and a series of high resistance shunts of from 7 to 20,000 megohms. The observed value of A is 230 times the theoretical value of Dushman—in disagreement with the recent theoretical work of Fowler and Nordheim. The discrepancy may be removed if the work function is assumed to decrease linearly (and only very slightly) with temperature, as suggested by Bridgman and Epstein. A decrease in the *photoelectric* work function of Pt with temperature has already been observed by the author (Phys. Rev. **29,** 451). Such a decrease also explains the linear relation between log A and b during outgassing. (See Phys. Rev. **31,** 236, 1928.) For palladium—outgassed, but probably not yet gas-*free*—the photoelectric and thermionic work functions appear to have a common value of about 5.35 volts, which value is enormously decreased by slight traces of hydrogen.

29. Superposition of x-rays. GERALD L. PEARSON AND WM. W. HANSEN. Stanford University. (Introduced by D. L. Webster.)—W. H. Watson (Proc. Roy. Soc. Edin., **45,** 48, 1925), working in the laboratory of C. G. Barkla, has performed experiments that seem to indicate that under certain conditions the effect of two x-ray beams passing through a silver film may not always be additive. The present research is a test of this point with conditions similar to Watson's, but with further refinements in accuracy of measurement. A silver film was exposed to two perpendicular x-ray beams: (A) from a tungsten-anode Coolidge tube and, (B) silver fluorescence rays excited by this same Coolidge tube. Intensity of the rays was measured as follows: (1) scattered by the silver film from beam A, (2) from B transmitted by the film, (3) combined scattered and transmitted. Intensity and quality of the primary beam was varied over a wide range by changing the voltage and by interposing aluminum filters. In all cases intensity (3) equaled intensity (1) plus intensity (2) within experimental error.

30. Recombination of ions in the chamber of an x-ray spectrometer. DAVID L. WEBSTER AND ROBERT M. YEATMAN. Stanford University.—It is usually assumed that for accurate comparisons of x-ray intensitites, the voltage applied to the ionization chamber must be sufficient to reduce the loss of ions by recombination to a fraction of the total number produced, less than the permissible error of measurement. Tests show, however, that under proper conditions the fraction lost may be independent of the total number produced, for any loss up to about 10%. With the chamber used here, this permits accurate comparisons of ionization currents with only 50 volts, instead of the 800 required to reduce the loss to 1%, and thereby minimizes errors due to battery changes. This constancy of the fraction lost, with different currents, probably indicates that the recombination is practically all columnar, as reported by other observers with alpha-rays. In the case of x-rays, columnar recombination must be recombination between ions produced by the same photoelectron. This condition must be satisfied best with faint rays, such as are used in x-ray spectrometry. With stronger rays it should break down, and *therefore these tests do not indicate anything about ordinary x-ray dosage measurement.*

31. The variation of the photoelectric effect with temperature, and a determination of the long wave-length limit for tungsten. A. H. WARNER, University of California at Los Angeles, California Institute of Technology.—The photo-current from clean tungsten has been found constant from room temperature to 1050°K with a long wave-length limit of 2720 ± 25A for this sample. The thermionic emission becomes measurable at 1050°. The photo-current begins to increase slightly here and is about 14% greater at 1160°. Beyond this point the thermionic current masks the photo-current. The target is a straight ten mil, non sag tungsten wire. The anode is a nickel cylinder, with guard cylinders on either side. The tube is of Pyrex with a graded seal to the quartz window. All leads are of tungsten. After a thorough outgassing the tube was sealed off the pumps. Magnesium was employed as a getter. The thermionic work function was used as a criterion of the cleanliness of the surface.

32. A preliminary examination of Langley's bolometric data on the solar spectrum. HAROLD D. BABCOCK. Mount Wilson Observatory.—Lack of laboratory data forced Langley to omit a discussion of the identification of the solar lines measured on his bolographs. Using modern photographic and bolometric results for laboratory spectra, his table of wave-lengths has been examined, especially in the region λ8500 to λ17000. The average deviation between Langley's solar wave-lengths and the corresponding values in the laboratory is 2 or 3A in the region now photographically accessible. Allowing some increase in this for $\lambda > 10500$A, provisional identifications are found for 43 lines in Langley's list, belonging chiefly to the lighter alkalies and alkaline earths, with a few lines of hydrogen, aluminum and metals of the iron group. From the abundance of the elements involved and the series relations of the particular lines, most of the identifications are obviously to be expected. The apparent absence of certain lines is explained. Assuming the identifications to be correct, the average uncertainty in Langley's list is about 4A for the region examined. For a few lines it is much greater. Further study of the Smithsonian results will be profitable.

33. On measurable functions of dynamical variables. BENEDICT CASSEN, California Institute of Technology.—In matrix mechanics the measurable variables of a dynamical system are represented by Hermitian matrices. If tH is the transposed matrix to H and cH is its conjugate, then if H is Hermitian, $tcH = H$. If K is another Hermitian matrix then $tc(HK) = t(cHcK) = tcKtcH = KH$ so that if HK is to be Hermitian we must have $KH = HK$. That is, if the product of two measurable variables is measurable, those variables must commute. As $tc(H+K) = tcH + tcK = H+K$, the sum of two measurable variables is a measurable variable. For a single particle, if $P_1, \cdots, P_4$ represent the momenta and $Q_1, \cdots, Q_4$ the coordinate then the most general measurable functions of these variables can be put in the form $f(P_1, \cdots, P_4) + F(Q_1, \cdots, Q_4)$ where f, F are any real functions.

34. Electric fields near the surface of tungsten wire of small diameter. C. C. LAURITSEN AND S. S. MACKEOWN, California Institute of Technology.—The thermionic current from tungsten wire of 0.00156 cm diameter was measured with electric fields as high as 2×10^6 volts per cm. From these data information regarding the electrostatic field existing outside a conductor could be obtained. The results indicate that for distances greater than 3×10^{-7} cm the magnitude of the field is given quite accurately by the image force equation, but that at distances less than this the field is smaller than that calculated from this equation. The field very close to the surface seems to depend upon the temperature of the wire, being less for higher temperatures.

35. An ultra-violet photometer. ROBERT C. BURT, R. C. Burt Laboratory, Pasadena.—An instrument is described which consists of a fused quartz photoelectric cell connected to a portable galvanometer and supplied with a series of filters of different cut-off limits. (2000A, 2540A, 3080A, 3220A, 3300A, 3350A). Due to the fact that the long wave-length limit for these cells is below the red, no correction need be made for different transmissions in the infra-red, of the filters. Also larger differences are obtained than if thermo-junctions are used. A thermopile is also described for use in calibration and for measurement of the total radiation.

36. On the widths of σ-type doublets in molecular spectra. J. H. VAN VLECK, University of Minnesota, and R. S. MULLIKEN, New York University.—These widths are calculated with quantum mechanics by one of the writers with two methods, using respectively Hund's couplings (a) and (b) as unperturbed systems. ^1P terms should exhibit a doubling varying as $j(j+1)$, and ^1D terms very weak doubling varying as a higher power of j, agreeing with Kronig's statement (Zeits. f. Physik, **46,** 820) that the effect is a perturbation of order 2σ. Including now the spin, the coupling between the components of s and l perpendicular to the figure axis induces transitions $\Delta\sigma_l=-2$, $\Delta\sigma_s=+1$ from $\sigma=\frac{1}{2}$ to $\sigma=-\frac{1}{2}$ in the angular momentum. If predominant this makes the $^2P_{1/2}$ state show a doubling varying as j, and $^2P_{3/2}$ only a higher order effect. This agrees nicely with experiment, especially in that wide multiplets (e.g. HgH), which involve relatively great coupling between l and s, show much greater doubling of $^2P_{1/2}$ than do narrow multiplets (e.g. MgH). The pronounced doubling of $^3P_0$ terms in wide triplets should be independent of j, as regardless of the rotation there are two different orientations of $s=1$ and l which give $\sigma=0$. The greater doubling of always the level with lower σ furnishes a convenient clue whether observed multiplets are regular or inverted.

37. The non-metastability of the 2s level in atomic hydrogen. V. ROJANSKY AND J. H. VAN VLECK, University of Minnesota.—The $2s$ level of H is generally considered metastable, as apparently the transition down to $1s$ violates the selection principle. However, Dirac's quantum theory of the electron shows that the $2s$ and $2p_{1/2}$ levels have exactly the same energy. Hence they form a degenerate pair, and may be scrambled together in an infinite variety of ways. In the absence of an external field any linear combination of their wave functions can be taken equally well as a proper solution of Schroedinger's equation, and only one out of an infinity of possibilities (viz., the one in which the coefficient of the $^2p_{1/2}$ part is zero) gives non-combination with $1s$. If the degeneracy is removed by a constant external electric field F, the $2s$, $^2p_{1/2}$ states are, in fact, transformed into a pair of levels whose separation is proportional to F and whose transition probabilities down to $1s$ are equal. The fact that absorption measurements of Ornstein, Zernike, and Snoek, Jr. (Zeits. f. Physik, **47,** 627) indicate $2s$ is not metastable, can thus be explained without supposing collisions of the second kind hurl atoms from $2s$ to $2p$ states. Because of the degeneracy of fine structure components with like j-values, the hydrogen spectrum should show a linear Stark effect even in weak fields, and this is calculated.

38. The ballistic method of ionization measurement with a quadrant electrometer DAVID L. WEBSTER AND ROBERT M. YEATMAN. Stanford University.—In the ballistic use of an electrometer, for ionization measurements, the chamber is exposed to rays for a predetermined time, and the reading ordinarily taken is that of the electrometer after it stops swinging. The present method, more strictly ballistic, is to read the farthest point of swing. This not only saves time, but avoids serious complications from insulation leakage. The validity of this method depends on 4 conditions: (1) linearity of the differential equation of motion; (2) its homogeneity, except for the term proportional to the ionization; (3) initial conditions, deflection and velocity zero; (4) constancy of exposure time. (4) is readily satisfied; (3) and (2) demand cancellation of natural ionization by a constant opposite current; (1) is the most questionable. The present tests, on an electrometer of 12 seconds period with exposures from 2 to 40 seconds, demonstrates the possibility of satisfying all these conditions, so that the strictly ballistic method has no systematic errors large enough to detect in the presence of a 1% erratic error. For large deflections, ballistic applications of a potentiometer show departures of about 1% from linearity, but even then, calibration by the potentiometer enables this electrometer to compare ionization currents accurately.

39. An extension to the photographic study of the infra-red solar spectrum. HAROLD D. BABCOCK AND W. P. HOGE. Mount Wilson Observatory.—Nearly fifty years ago Abney photographed absorption lines in the solar spectrum out to λ9867. Although the bolometric observations of Langley and Abbot reveal hundreds of lines beyond Abney's limit, no photographic record appears to have shown them. Using emulsions containing neocyanin prepared by Dr. C. E. K. Mees, the coarser features of the solar spectrum have been photographed out

to λ11760 with a prism spectrograph, yielding measurements on 25 lines beyond λ10000. With a concave grating giving a dispersion of 4.75A per mm, 52 lines have been measured between λ9867 and λ10925. A new region over 1000A wide is thus photographically accessible with instruments of greater resolving power than that previously used in the infra-red, while with low power spectrographs nearly 2000A can be added to the photographic range. The study of this region is part of a detailed examination of the solar spectrum beginning at λ6900 which is now in progress, in the course of which nearly 400 lines previously unrecorded have already been measured. The fourth member of the Ritz-Paschen series of hydrogen, λ10049, has been positively identified in the sun, where it is wider than $H\alpha$, though probably not so black.

40. The function of a horn in acoustics. MARCUS O'DAY, Reed College.—Webster, in laying the basis for his theory of horns, sets up the equation of continuity for a varying cross-section but uses the ordinary equation of motion $\partial p/\partial x+\rho\partial u/\partial t=0$. Here p = pressure, S = cross-section, u = particle velocity, ρ = density. The writer points out that this is a point relation and that by the same method as used by Webster for derivation of the equation of continuity, he gets as the equation of motion $\partial(pS)\partial x+\rho\partial(uS)/\partial t=0$. Elimination between this and the equation of continuity gives as the equations of propagation $\partial^2(pS)/\partial t^2=c^2\partial^2(pS)/\partial x^2$ and $\partial^2(uS)/\partial t^2=c^2\partial^2(uS)/\partial x^2$. Thus for an infinite horn the amplification is independent of the particular manner in which the horn flares. The function of a horn therefore seems to be that of a pure resonator.

41. Interference of reflected light. PAUL S. EPSTEIN California Institute of Technology. It is well established that the molecules, atoms or free electrons of a mirror casting back light are in a state of molecular agitation. We are, therefore, inclined to expect this motion to influence the reflected light. If the incident light is of high spectral purity the thermokinetic effect of the mirror might decrease the purity and make the range of interference shorter. An experiment recently tried by Rocard and de Rotschild had, however, a negative result: after six reflections from a silver mirror the range of interference was not appreciably reduced, though these physicists expected it to fall to one fourth of its original value. In view of this a theoretical investigation of the properties of reflected light was undertaken. A straightforward computation leads to the result that molecular agitation has no influence either on the frequency or the phase of reflected light, provided that the reflecting layer is thin compared with the range of interference. The result of Rocard and de Rotschild is, therefore, in agreement with theoretical predictions.

42. Photoelectric control with mirror reading instruments. KARL LARK-HOROVITZ AND GEORGE W. SHERMAN, Purdue University.—Constancy of a measured quantity is maintained by using mirror reading instruments combined with photoelectric (or selenium or Thalofide) cells in the following arrangement: a beam of light of a certain width is reflected from the mirror unto a photoelectric cell; any deviation from a definite position through fluctuations in the quantities measured cause changes in photoelectric current (p.c.). These changes in p.c. operate by means of a triode a relay and start mechanical devices compensating the fluctuations. The cell is shielded by a plate with three divisions: one side being completely transparent, the other side being completely light tight, whereas the middle part allows only one half of the incoming light to pass through. The photoelectric cell is placed so that the position of the mirror to be maintained corresponds to the middle part of the plate; deviating to either side cause then changes of the p.c. in opposite directions. Using a Weston "zero center and galvanometer" relay one single cell is then sufficient to compensate fluctuations in any direction correlating in a unique way deflections of the mirror and p.c. The temperature of electric furnaces has been controlled with thermocouple and galvanometer: an actual fluctuation of 80°C (at 600°C) was eliminated to less than 1°C. The high tension in an x-ray circuit can be controlled using a high tension electrometer with the cell to regulate the primary impedence compensating any fluctuations occurring on the high tension side.

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